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The Materials for Dye Kettle Construction as Related to

The Economical Production of True Shades

By HENRY BARKER BURKE

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IN THE practical application of dyestuffs much time and waste is common throughout the textile industry by reason of ignoring or minimizing the effect of using dye kettles of a porous dye absorbing construction or of such construction as may alterably affect the dyestuffs used therein to an extent that the true shade is either never developed or produced, or in special cases developed or produced only through adherence to troublesome and costly procedure involving the use of further chemicals to compensate for or protect against the deleterious effect of the material entering into the kettle construction.

When the chemist is required to make a dyeing of a certain color he will carry out an exact procedure, with definite weights of material, dyestuffs, and suitable chemical assistants. He will, moreover, do the actual dyeing in some utensil which is non-porous and which will exert no influence upon the final result. He can be reasonably certain of obtaining a true shade and of repeatedly duplicating the results so obtained.

Textile executives, as well as experienced textile chemists and dyers have for the most part long been aware of the difficulties and increased cost of procedure confronting them in any attempt to produce a true shade in kettles of a dye absorbing construction. And many attempts have been made within the industry to correct or at least improve the dye kettle in respect to this objectionable feature (color absorption).

The immediate suggestion, of course, was to simulate laboratory practice and use glass or porcelain. To an extent this is practical (certain small parts), but the records do not disclose any practical applications of such material in vat construction beyond that which must definitely be ascribed to experimental work. Carefully surfaced as well as specially surfaced concrete (ground glass) has been tried but without noteworthy results.

Next, attempts were made to achieve the end in view (dyeing to a true shade) with metal lining on wood, or even an entire vat of solid metal. But at this point, the second factor (the effect of the material used for construction on the final shade) appeared to have apparently a more devastating effect than the absorption of color by the material used in the vat construction.

Most metals in contact with the dyebath exerted a decided influence upon the final shade, so much so that practical dyers were definitely aligned against not only the use of any all-metal machine, but of having any metal present in the dye compartment.

The common practice was to reserve a kettle for a particular range of shades and to so arrange the dyeings of the day that they ran from the lightest to the darkest. In this manner, the difficulties of one shade picking up color from that absorbed by the kettle in the dyeing of a previous shade was minimized and was taken into account in the color matching. Most executives had endorsed this as the most practical solution of continuous dyehouse productions of true shades.

Of course, through this development it was found that certain special phases of dyeing could be applied in contact with certain metals with satisfaction. That is, certain classes of dyestuffs as a whole gave favorable results in contact with certain metals, or at least the true shade was not modified beyond that acceptable to the trade. By example, cast iron construction for sulfur blacks, heavy shades of direct colors, plain or developed, logwood blacks, etc.; bronze, mostly for parts in connection with acid dyeings; copper for vat linings with acid colors, especially in the silk trades where the smoothness of the surface of the vat was of primary importance in relation to the physical condition of the finished material; German silver, mostly for parts, and so forth.

But as pointed out, even in these instances, the utilitarian considerations far outweighed that of precision or

accuracy in obtaining a true shade. In short, as expressed by the dyer, "Metals have a saddening effect on the dyestuffs," and a very cautious attitude obtained as related to the application of dyestuffs, not alone in metal vats but in having any excessive amount of metal present in the dyebath.

With the introduction of Monel metal to the textile trades as a dyehouse metal applicable alike for linings or parts, there was a revival of interest in metal dye kettle constructions. This metal had a high resistance to acid and alkali, in all concentrations commonly met with in the dyehouse, and although it had definite limits as related to its influence on dyestuffs, it so excelled previous metals or alloys employed as to have a wide and extended use.

Its success prompted the development of many alloys designed or heralded by their proponents as perfect dyehouse metals, but prior to the introduction of monel, the metallurgists gave little or no direct attention to the development of alloys to satisfactorily meet the conditions imposed in textile coloring. And since that time, while there has been a very definite progress in the development of alloys of various metals to withstand the action of chemicals common to industrial practice, the burden of selecting the alloy most appropriate for a specified textile activity has been left to the manufacturers of equipment. Some of the more progressive manufacturers of equipment have carried out carefully regulated experiments at considerable expense to themselves and have accumulated very comprehensive data pertinent to textile applications, especially as related to the most suitable metals and alloys for the production of true shade dyeings.

More recently, through advances made in other fields (metal trades) there has been developed alloys of marked utility to the textile industry in its chemical and dyeing departments. Of especial interest to the textile world for purposes related to the dyeing and finishing processes is the development of the aluminium-manganese alloys and the aluminium-bronze alloys and the nickel-chromium steels of the "stainless" types and to a lesser degree nickel steels and even pure nickel. Also there has been a marked advance in the development of plastics, both laminated and hot pressed, and such products have been widely used abroad for dye kettle construction.

The importance of obtaining a true shade dyeing has been long recognized and cannot be over emphasized. This brief survey of progress leading up to a more uniformly dependable kettle is made to acquaint and familiarize in a non-technical way those whose interests lie in this direction, with the latest accomplishments in this field.

It should be borne in mind that the various metal alloys have been designed very largely to meet conditions as imposed by the metal trades and that the representatives of the metal companies are rarely conversant with the demands of the textile chemist and dyer. In like manner, the textile chemist and dyer have seldom any appreciation of the properties and values of interest to the metal trades and will in all probability lack entirely the shop-man's point of view. However, correct shop procedure in fabrication may and, in fact, does prove as essential as the choice of a metal in terms of durability and reliability of the finished kettle. By this is meant not so much the design as the treatment and methods used to work the metals.

Of the alloys commonly recommended to the textile trades for use in the chemical and dyeing departments few chemists and dyers (and few mill engineers) have knowledge of the percentage composition of the alloys. Since it may be generally stated that the difference in shop metals is chiefly a chemical one, and their physical characteristics vary according to the proportioning of their chemical ingredients a few analyses should be of interest.

	Low-Carbon Machinery Steel	*High-Carbon Tool Steel*
Carbon	0.15%	1.00%
Manganese	.40	.60
Silicon	.01	.15
Phosphorus	.07	.03
Sulfur	.05	.03
Pure Iron	99.32	98.19
Tensile Strength	60,000 lbs.	120,000 lbs.

Here we have the five chemical elements common to all irons and steels. The sensitiveness of the final product to slight differences in amounts of these elements can be seen in the doubling of the tensile strength.

Now compare the following nickel steels which are designed primarily for case hardening and used for such parts as differential gears, wrist pins, transmission gears, tappet, etc.

Carbon Range	Manganese Range	Phosphorus Max.	Sulfur Max.	Nickel Range
.10-.20%	.30-.60%	.04%	.045%	3.25-3.75%

Balance iron

Of course, this is simply an illustration of type, there being many variations to produce some specific characteristic, as machinability, case hardening, toughness, etc.

The nickel-chromium steels would be proportioned in a range something as follows which represents the 3100 S.A.E. series.

Carbon Range	Manganese Range	Phosphorous Range	Sulfur Range	Nickel Range	Chromium Range
.20-.55%	.50-.80%	.04—%	.045—%	1.-1.5%	.45-.75%

Balance iron.

Now compare this with a typical formula for "Stainless Steel" which has a high resistance to acid reactions and has been widely used in textile mills for dyehouse equipment.

Carbon	.15%
Manganese	.40-65%
Phosphorus	.035% Max.
Sulphur	.035% Max.
Nickel	8.00% to 9.5%
Chromium	17.5 % to 19.5%
Balance Iron	

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Rayon Dyeing and Finishing—7

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Consulting Textile Chemist

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CHAPTER V—DYEING AND FINISHING OF CIRCULAR KNIT RAYON FABRIC

(Continued from page 327, May 22 issue)

Scouring Troubles and Methods of Avoiding Same

Improper scouring sometimes causes so-called "soap spots" to appear in finished fabric. These spots are usually due to the presence of a mixture of calcium and magnesium soaps dissolved in mineral oil. The direct cause often is the presence of an unusually large amount of mineral oil in a given batch of fabric, or the presence of an unusually large amount of soluble calcium and magnesium salts in the water on the particular day the trouble is encountered.

Soap spots may be prevented by careful attention to the condition of the dye bath as they are only possible in so-called "broken" bath. The addition of alkali, soap, and especially a solvent containing material, to the scouring bath shortly after such a bath begins to "break" will often prevent the formation of objectionable soap spots on the goods.

It sometimes happens that small white spots, known as "chalk marks," are visible on finished circular knitted fabric. Close examination of these spots will usually disclose the presence of broken filaments which indicate rough treatment at that particular spot. They are caused by a combination of two factors:

(1) Softening of the fabric due to the presence of alkali in the bath.
(2) A rubbing action, due to a poor surface inside the wet treating machine, or due to a tangled condition that sometimes occurs during the scouring or dyeing processes.

Once these marks are on a fabric they cannot be removed, although they can be somewhat hidden by means of an oiling treatment. Such a treatment may be applied in the following manner:

(1) Saturate a rag with a mixture of oil dissolved in a solvent.
(2) Rub the spot lightly with the oiled rag, taking care to brush towards the center in order to avoid the formation of a ring of oil at the outside edge of the treated spot.

There are two means of reducing the quantity of chafe marks. One consists of the reduction of the alkaline strength of the solution. This is best done by substituting a milder alkali for the one used, rather than by reduction of total alkali content of the solution.

The second means, which is the better of the two, is careful attention to proper loading of the dye kettle. When a kettle is not overloaded, and when every roll is of approximately the same length, there is no reason why the rolls should tangle. Unless the rolls become tangled during the scouring and dyeing operation there is no reason for chafe marks to be formed.

SCOURING PROCEDURE

Due to variations in the local conditions from plant to plant, as well as the variations in the fabric processed and in the results desired, it is impossible for all plants to use the same scouring procedure, or for the same procedure to work equally well in all plants. Nevertheless the general scouring practice is approximately the same throughout the circular knit rayon industry, the variations being in intensity and time of treatment.

Some plants endeavoring to produce a finished product considered suitable for the production of low priced garments at the lowest possible cost for the dyeing and finishing operation, scour and dye in a simgle bath with a moderate degree of success.

Due to the presence of large quantities of oil in circular knit fabric, a simultaneous scouring and dyeing treatment has given so much trouble in most plants that this practice has been abandoned in favor of the more efficient two bath treatment. However, some plants still operate under a single bath process, a typical example of which follows:

Typical Single Bath Process for Simultaneous Scouring and Dyeing of Circular Knit Rayon Fabric

(1) Load machine.
(2) Fill with cold water.
(3) Add scouring ingredients as follows:
Per 100 *lbs. of fabric*:
3 lbs. soda ash
5 lbs. low grade soap
2 lbs. "soluble pine oil" or similar solvent containing material
(4) Turn steam on full and raise kettle 160° F.
(5) Add dyestuff to front of kettle.

This process necessarily presupposes the use of extremely level dyeing colors, regardless of the fastness properties of the same.

The dyestuff is added slowly, dipper by dipper, by an operator who allows a small stream of dyestuff to trickle from the dipper to the machine while the dipper is moved from side to side of the machine.

(6) Run until the desired shade has been attained.

(7) Extract and dry as usual.

The above procedure is not to be recommended as it results in the production of an excessive amount of soap spots as well as a finished product containing a relatively large amount of the original rayon lubricating oil. The presence of this oil often gives garments made from such a fabric an objectionable odor. When present in a sufficient quantity it causes paper and paste board boxes in contact with the same on merchants' shelves to become seriously stained, thus presenting a very poor sales appearance.

The simultaneous scouring and dyeing procedure given above has fortunately been largely replaced by the more desirable two bath process. Although the scouring treatment given the goods before dyeing varies appreciably from plant to plant, the following procedure is typical of the best accepted practice during 1930:

Typical Scouring Procedure for Circular Knit Fabric

(1) Run water in kettle (temp. 80 to 120° F.) using minimum amount that will enable the fabric to run freely over the reels. A properly loaded kettle of the correct type requires approximately a 20 to 1 bath.

(2) Load kettle with fabric.

(3) Add 2 lbs. soda ash or tri-sodium-phosphate (depending upon water conditions).

(4) Turn on steam and run goods for 10 minutes.

(5) Add 3 lbs. high grade neutral soap—olive or red oil base.

(6) Add 2 lbs. "soluble pine oil" or a similar solvent containing material. If desired this solvent material and soap can be added simultaneously in order to aid solvent dispersion.

(7) Raise bath to boil. Observe condition of bath at all times. If bath does not show a good, clean, sudsy condition, add more soda soap and pine oil. It is impossible to accurately predict the amount of soda soap and solvent or the exact proportions of the same that will be required under an unknown set of conditions.

(8) Run the kettle at or near the boil for one hour.

(9) Drop bath and proceed with bleaching or dyeing operation.

DISCUSSION OF BLEACHING

Circular knit rayon fabric is bleached for two distinct and different purposes. First and most important is the production of a three-quarter bleach in the fabric in order that light shades, such as pink, orchid, nile green and baby blue, will appear brighter and more pleasing to the eye.

A small quantity of fabric is given a "full" bleaching treatment in order that the fabric may be sold as white goods. The constant demand on the part of the purchasers of circular knitted garments for pure white bleached garments has often resulted in excessive bleaching treatment on the part of the dyer and has caused a large quantity of over bleached fabric to appear on the market—particularly in men's wear. The poor service given by this over bleached fabric has effectively lessened the market for full bleached circular knit rayon fabric and has unfortunately curtailed the use of rayon in men's wear.

A large proportion of all bleaching of circular knitted rayon fabrics is done with sodium hypochlorite solution because of its low cost. Hypochlorite bleach is the easiest, cheapest and most satisfactory method of bleaching circular knitted rayon fabrics.

Active chlorine used in bleaching is today purchased by dyers in the two following forms:

(1) As sodium hypochlorite solution.

(2) As liquid chlorine.

Mills operating in or near a large city find it economical to buy sodium hypochlorite as a concentrated solution containing 14 per cent available chlorine and not over 1 per cent free alkali.

This solution is easily obtained in large cities and is distributed daily to laundries and dye houses in tank trucks. Competition has reduced the cost of this solution to a price below that at which small quantities of sodium hypochlorate solution can be manufactured within individual dye houses.

Mills operating in rural regions find it economical to buy liquid chlorine in large cylinders and to manufacture their own sodium hypochlorite solution, allowing chlorine gas to slowly react with a solution of soda ash, caustic soda or both.

For this purpose it is customary to use a cement tank fitted with a perforated lead coil to which a cylinder of liquid chlorine is connected. A very satisfactory sodium-hypo-chlorite bleaching solution can be made in the following manner:

1. 350 lbs. of soda ash is dissolved with 400 gallons of water.
2. 100 lbs. liquid chlorine is added to the solution slowly from the above mentioned perforated lead coil. Care must be taken that the temperature of the bath is low at all times in order that only sodium-hypo-chlorite be produced.

There are so many methods of successfully producing three-quarter bleach as a base for bright shades that it would entail needless repetition to list them here.

The most radical procedure is one involving the use of sodium-hypo-chlorite solution at a temperature of 180° F.

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Oxycellulose and Hydrocellulose

Their Detection, Properties, and Probable Differences in Constitution*

By H. A. THOMAS

PERUSAL of the extensive available literature devoted to the study of the so-called oxycellulose and hydra- or hydro-cellulose reveals indisputably that these terms do not apply to chemical individuals but to mixtures of cellulose degradation products. The properties ascribed by different investigators to these two materials vary to a greater or lesser degree, indicating that different mixtures are being dealt with although they are identically designated. This laxity in terminology has naturally led to much confusion. A. Girard introduced the term hydrocellulose for the material obtained by degradation of cotton with acids[1] and for a time, material produced in the manner described by Girard was known as "Girard's hydrocellulose." The material produced by treatment of cotton with organic acids and also by more severe treatments with mineral acids also became known as hydrocellulose. Similarly, materials obtained from cotton by mild oxidations with sodium hypochlorite in the presence of sodium carbonate and also in the presence of acid, are all termed oxycellulose. C. F. Cross and E. J. Bevan realized the undesirability of this loose terminology, and preferred to speak of the oxy- and hydro-cellulose processes, rather than apply these terms to the products obtained.[2] It is therefore desirable that a new terminology which is more precise and descriptive be introduced; with this objective a suggestion is made at a later stage in this paper, but at the present stage the old terms will be employed.

The production of "oxycellulose" in fabrics, caused by a too drastic hypochlorite bleaching process, was first observed by G. Witz[3] and commented on by Cross and Bevan, who examined the nature of the chemical processes occurring.[4] Besides the oxidation treatments mentioned above, the combined action of sunlight and air (presumably a photo-chemical reaction), or of caustic soda and air during kier-boiling operations, also produces oxycellulose in cotton. The various types of oxycellulose encountered have been described by C. Birtwell, D. A. Clibbens, and B. P. Ridge,[5] who show that there are two extreme types: (1) characterized by a great affinity for methylene-blue, and abnormal retentive power for alkali, (2) characterized by a high reducing power and an excessive loss in weight by scouring. A comprehensive survey of the various results obtained from studies of hydrocellulose has been made by P. H. Clifford.[6]

Most hydrocelluloses investigated appear to possess the same characteristics, viz., a marked reducing action, a high copper number, and a low viscosity when in cuprammonium solution; they can also be more readily acetylated than can cellulose itself. This enhanced reactivity also appears to apply to oxycelluloses, which usually exhibit strong reducing properties, possess a high copper number, and give low-viscosity cuprammonium solutions; most oxycelluloses possess a marked affinity for basic dyestuffs but a poor affinity for direct cotton dyestuffs, although it appears that some oxycelluloses described in the literature do not exhibit these peculiar dyeing properties.

Several tests for the detection of oxy- and hydrocellulose have been published, and most of them are based on the reducing properties of the two substances; such tests are not therefore discriminatory between the two degraded celluloses. Both oxycelluloses and hydro-celluloses reduce Fehling's solution to give a red precipitate of cuprous oxide, or a solution of cupric thiocyanate to give a precipitate of cuprous thiocyanate, and reduce ammoniacal silver nitrate solution to silver. Some specific tests for oxycellulose have been described in the literature, and were examined for their efficacy in this present investigation.

A standard oxycellulose material was prepared under controlled conditions by a treatment of normal bleached cotton piece with sodium hypochlorite solution in the presence of a little sodium carbonate. A standard hydrocellulose was prepared in two ways by the controlled treatment of normal bleached cotton piece with hydrochloric and also sulfuric acid, as described in the experimental section of this paper. Both the oxy- and hydrocellulose materials were moderately tender and readily reduced Fehling's solution.

The stannous chloride-gold chloride test of R. Haller[7] was then applied to a piece of oxycellulose material,

* This paper was read before the Manchester Section on April 7 and is reprinted from the Jour. Soc. Chem. Ind.

hydrocellulose material, and normal white cotton piece as a control. The three materials were immersed in a 1% solution of stannous chloride for 1½-2 hours at room temperature, rinsed, and then immersed in a very dilute solution of gold chloride. The purple coloration was obtained on the oxycellulose, but the test did not give consistent results when repeated; frequently the cotton piece and hydrocellulose material became almost as purple as the oxycellulose material. The test is also rather tedious and expensive for routine testing, but is based on a very important principle, namely, the affinity of oxycelluloses for metals from solutions of their salts.

The "heat test" described by M. Fort[8] was found to be difficult to apply. Although the most satisfactory temperature recommended, 175-190°, was employed, it was found that the hydrocellulose material became discolored to the same extent as the oxycellulose. This is rather to be expected, since both materials employed contained degraded cellulose products and consequently charred more readily than normal cotton. The methylene-blue test was found to be fairly satisfactory, though not strictly specific for oxycellulose, since although this material became deeply colored when immersed in a dilute solution of methylene-blue, the hydrocellulose material and normal cotton piece became quite noticeably colored, and grey cotton also becomes deeply colored. A negative test for oxycellulose with direct cotton dyestuffs was also found to be fairly satisfactory, but was not selective enough since, even with some of the most suitable direct dyestuffs for the purpose, the oxycellulose became colored to quite an appreciable extent, and the hydrocellulose had a somewhat reduced affinity for the color. New selective positive tests for oxycellulose were therefore devised and were based on the enhanced affinity of the oxycellulose material for metals from solutions of their salts. The best conditions for selective reactions with oxycellulose material were worked out, and it was found that solutions of iron salts gave very satisfactory results, lead salts were quite suitable, but copper salts did not give such discriminatory results. Immersion of the oxycellulose, hydrocellulose material, and white cotton piece in a solution of ferrous sulfate, followed by rinsing, and subsequent immersion in potassium ferricyanide solution, resulted in the development of a deep blue coloration of the oxycellulose material, but only very slight tinting of the cotton and hydrocellulose material. In a similar manner a deep blue color is developed on the oxycellulose but not on the hydrocellulose or cotton by immersion in ferric chloride solution, rinsing, and subsequent development in potassium ferrocyanide solution.

Another selective test was evolved on the basis of the production of lead chromate by immersion in a lead acetate solution and subsequent treatment in a solution of sodium chromate. The reducing power of oxycellulose, combined with its affinity for metals, furnishes a further selective test; thus, on immersion in ferric chloride solution, a certain amount of reduction to the ferrous condition occurs on the oxycellulose material and probably on the hydrocellulose. On rinsing, however, the iron salt is removed from the cotton and hydrocellulose material, but iron in the ferrous condition, and probably also in the ferric condition, is fixed on the oxycellulose material, so that a deep blue coloration is obtained on immersion in a solution of potassium ferrocyanide. Immersion in copper sulfate solution, followed by rinsing and subsequent immersion in a solution of diethyl dithiocarbamate, resulted in a deep brown coloration on the oxycellulose material but also gave a distinct brown coloration on cotton and hydrocellulose, though considerably lighter than that on the oxycellulose material. The best conditions for the selective tests for oxycellulose material are given in the experimental portion. It must be emphasized that in order to obtain the best results, the directions set out should be followed rigorously; thus, it is extremely important to rinse the material thoroughly between the immersion in the first solution and in the development bath, in order to ensure that the test shall be of good selectivity. Boiling the material in Fehling's solution was found to be a good test for both oxycellulose and hydrocellulose, when it was performed under the most satisfactory conditions, a dull red color developing on both oxycellulose and hydrocellulose material, but not on the white cotton piece. The presence of hydrocellulose in a fabric is inferred if such a coloration is obtained, and the metallic affinity tests indicate that no oxycellulose is present. It seems probable that no qualitative positive selective test for hydrocellulose in the presence of oxycellulose and cotton can be evolved, since hydrocellulose behaves either in a manner similar to cotton cellulose or in a manner similar to oxycellulose. The application of the tests to material containing grey cotton and also to dyed cotton has been investigated, and a general procedure is recommended in the experimental section, including methods of stripping dyestuffs from the fiber without vitiating the tests. It has been found that differences in the twist of yarn do not affect the selectivity of the tests.

The dyeing properties of the oxycellulose and hydrocellulose materials have been thoroughly investigated with representatives of basic dyestuffs, direct cotton dyestuffs of the stilbene, monoazo, diazo, and trisazo types, sulfur dyestuffs, and vat colors of the indigoid, anthraquinone, and sulfurized classes. Basic colors have a much greater affinity for the oxycellulose than for the hydrocellulose and cotton, but if the three materials are first mordanted with tannic acid fixed with tartar emetic, the same depth of shade is obtained on each; a solid shade can therefore be obtained on cotton material containing both oxycellulose and hydrocellulose, by dyeing with basic dyestuffs on a tannin mordant.

Direct cotton dyestuffs have a much diminished affinity for the oxycellulose material than for cotton or the hydrocellulose material. Both basic and direct cotton dyestuffs have a slightly diminished affinity for the hydro-

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PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

JUNE 5, 1933

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UNEMPLOYMENT REGISTER

For Members of the A.A.T.C.C.

At the last annual meeting it was suggested that the Association conduct an Unemployment Register for its members.

In accordance with this suggestion, members who are without employment at the present time should forward to the secretary a statement as to their qualifications and experience. This information will be placed on file and subsequently published in these pages. Identifying key numbers will be used so that each case may be brought most effectively to the attention of those persons likely to be in need of men of the stated qualifications.

Employers are also requested to file with the secretary any opportunities which are available in their businesses.

It is to be understood that this Unemployment Register is not (at the present time, at least) to be used for the benefit of those now employed and who are anxious to improve their conditions.

A. NEWTON GRAVES,
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APRIL MEETING, NORTHERN NEW ENGLAND SECTION

THE third meeting of the Northern New England Section was held April 6th as a joint meeting with the Boston group of the Rubber Division of the American Chemical Society. Mr. S. G. Byam of the E. I. du Pont Co. presented a paper entitled "Problems of the Rubber Proofing Industry," and Mr. E. M. Hayden of the Stanley Chemical Co. presented a paper on "Lacquer and Its Uses." At the dinner, prior to the meeting, Mr. Seaverns of the Howe & French Co. gave an entertaining and instructive ten minute talk on "Liars and Thieves." The total attendance of 120 from both groups was very gratifying to the committee in charge.

Proceedings of the American Association of Textile Chemists and Colorists

Problems of the Proofing Industry*

By S. G. BYAM

Rubber Chemicals Division, E. I. du Pont de Nemours Co.

IN VIEW of the fact that we have the pleasure of having the New England Textile Chemists meet with us, my remarks on rubberized fabric problems are directed mostly to the textile angle of the industry. In this connection, I am directing your attention first to these charts which summarize the production of rubberized fabrics over the past twelve years. It will be noted that the total fabrics used in 1929 is estimated at 75 million yards, an amount which we believe can be further increased if the ingenuity of the textile manufacturers and proofers is exercised in the future as it has been in the past.

It is believed significant that the production of proofing proper, auto top being excepted, has shown a drop from the 1929 level of only 25% in 1932 and is still 20% above the average of the 12-year period. The trends shown in the various charts are interesting but need no particular comment, except to point out in Chart No. 3 the increased popularity of double texture raincoat and decreasing use of single texture during recent years.

One cannot discuss proofing problems without emphasizing the importance of having fabrics free of injurious chemicals such as copper and manganese. This problem was discussed in detail in 1928 with our textile friends when a specification for fabrics to be rubberized was formulated. The limits set at that time were .002% of copper and .001% of manganese which were considered almost impossibly low by the textile people but not needlessly so by the rubberizers. Experience in the past 5 years has shown that these limits could be consistently met by the fabric dyers and we must thank them for their excellent cooperation. In spite of the attainment of this goal, I would go one step further and ask the textile manufacturers to work for the complete elimination of copper and manganese in fabrics to be rubberized. As long as any of these ingredients are present, a hazard exists for the proofer for they always exert a harmful effect on rubber. Even if we can prolong the life of our product with modern accelerators and anti-oxidants, we cannot nullify the effect of copper. We have enough variables in proofing production with our erratic dry heat ovens and mediocre sulfur chloride cures without having to worry about copper and manganese. I am far from convinced that completely copper- and manganese-free dyed fabrics are impractical and ask for the proofing industry that the textile chemists continue their fine work toward elimination. It should be mentioned that iron in the form of ferric sulfate particularly should not be present, as it has a high acid value with a consequent retarding effect on rate of cure and accelerating effect on oxidation.

Raincoat—or more properly, garment fabrics—are the largest class of proofed goods and include today practically every type of product that has ever been used for this purpose. They include gas mask type, lightweight bombazine, leatherette and its rough-wear modifications, ripple surface or elephant hide, double texture trench cloth and jerseys, suede cloth, latex, etc. In fact, there are too many types in vogue for most economical manufacture and production. We need to reduce this array and concentrate on a few new effects, in which the textile industry can doubtless help us greatly. A new facing fabric for double texture to replace jersey of which we are sick to death would be desirable for one. This should appeal to textile suppliers as every yard of double texture calls for two yards of fabric.

Single texture proofed goods are finished with corn and potato starch, mica, shellac and casein water varnishes, oil varnish and nitrocellulose lacquers. I am glad Mr. Hayden is here to tell us in detail about lacquer and how it may be best anchored to rubber. Powdered glass has also been

*Presented at meeting, N. N. E. Section, April 6th.

used as a decorative finish as have transparent globules of silica and synthetic resin in solubilized gelatin. This last use was patented in England (No. 348169) in 1930. Design and texture are also important in decorative effects and are provided by printing or art-proofing, transfer processing, embossing and souping and by utilizing in various ways novel weaves and constructions of fabrics. Perhaps some day we will turn to advantage the light-sensitive characteristic of anti-oxidants which now represents their chief disadvantage in light colored rubber.

The imperviousness to water and air of rubber constitutes not only an important virtue of the raincoat but also a serious disadvantage. We all know how hot and uncomfortable a raincoat becomes in hot weather. The Aztec Indians at the time of the Cortez invasion were found to be wearing protective garments made of fabric smeared with latex and also cloaks closely covered with feathers. Even today, the Chinese and Japanese use rainwear made of straw. Garments of these types shed water readily and permit free passage of air to the body. It is quite possible to make a rubberized fabric that is porous enough to breathe and yet shed water readily by properly impregnating a napped or filled fabric with rubber or by incorporating flock in a rubber cement. Perhaps this offers a possibility for a new raincoat.

Another problem that needs attention pertains to the roughwear type sport and work coats, etc. Very attractive simulations of leather are made which have wearing qualities equal to and exceeding those of leather, but to my mind they usually lack the important quality of pliability, though they are flexible enough in any one direction. Sheet rubber and uncoated fabric are definitely soft and pliable but coated fabrics, other than very thin materials, tend toward boardiness. This may be a function of the coating process and again may depend on the fabric construction. A pleasing degree of pliability exists in the material known as Elephantide which is made by calendering a film of rubber on the fibers of a napped fabric. Unfortunately this particular type suffers from a tendency of the coating to peel due to its meager anchorage to the nap. Still, perhaps it is a lead for the proofers and fabric manufacturers to follow if they consider pliability of any importance.

There has been some publicity given to the remarks of Professor Laird of Colgate about the bad odor of rubber. This professor goes so far as to characterize the odor of rubber as a stench, ranking it with that of garlic and perspiration in unpleasantness. While I do not agree with this and I do not believe you do, we must admit that decomposed and burning rubber gives off a foul odor. We also know that improperly neutralized sulfur chloride cured goods and rubber containing certain accelerators smell anything but pleasant. We must, therefore, recognize the problem of odor and make sure that raincoats and other proofed goods which may have even more personal uses are neutral in odor or have a distinctly pleasant smell, lest any sales resistance due to occasional bad smell result. Deodorants and reodorants are becoming more evident in the market and perhaps the proofer and textile manufacturer can utilize them to their advantage.

Operating Problems

In addition to the product problems mentioned, the proofer is confronted with many operating problems that often cause considerable annoyance, to say nothing of expense. We are mentioning a few of these in the hope that they will suggest a discussion by those present. In making calendered coated fabrics it is often difficult to obtain the perfectly smooth, glass-like surface, which is the goal of every calender operator. Pitted calender rolls, poor dispersion in mixing, improper heat on the calender or warm-up mill and many other things contribute to a poor surface. The calender must, of course, be smoothly ground and have the proper crown for the type goods to be handled. The stock must be well mixed, and must withstand calender temperatures without scorching lest streaks of burnt stock appear. Proper softeners should be used, and care must be taken with their selection to be sure they do not produce the cloudy spots or "fish tails" that sometimes appear. Bubbles and air blisters may be due to too much or too little heat, and sometimes are avoided by a needle roll or by passing the film over an air bar before applying it to the fabric.

To obtain good anchorage of rubber to fabric it is necessary first of all to start with fabrics having a soft finish, as free as possible of sizing ingredients. If the goods are calendered, a base spreader coating is desirable. This base coat should be colored to approximately match the color of the fabric so that if it is pushed through the weave of the fabric by the subsequent calender or spreader knife pressure it will not be too readily apparent. If the fabric has a pronounced design the base coat should match the predominating color and should be dense or opaque enough to prevent the form of the design showing through on the face of the coating. This is particularly necessary with spread goods where the coating is rather thin. The dyes and colors used in printed fabrics must be insoluble in rubber as well as in water to prevent migration through the rubber film and their appearance on the face.

We have mentioned previously the problem of pliability which is of concern to the proofer not only in rough wear fabrics, but also in the common double texture. These fabrics are all too often boardy and stiff. Probably one of the chief elements of attraction of the double texture jersey raincoat has been its pliability as compared with that of the trench cloth or combined gabardines and twills. Apparently softness is a function of fabric weave to quite an extent, though the rubber compound itself must be

properly made. Softeners such as brown factice and the cumars in particular are valuable in this connection. Latex coatings may provide a partial answer to this problem as they give exceptionally strong combining in thin films. Latex films, however, tend to be stiffer than films from crude rubber cements of similar loading. I think, however, that construction and weave of the fabric—and perhaps the method of application—are the chief factors of softeners.

When fabrics are spread, the cements should be made with solvent containing a minimum of high boiling fractions. Complete drying is necessary for quality as oily residues in sulfur chloride cured goods in particular will be detrimental. The rate of evaporation of the solvent on the spreader is one of the determining factors of economy of spreading for one cannot run a spreader faster than the solvent can be dried out. Long spreaders, forced drafts, enclosures and other means are sometimes used to get rid of solvent. Usually a 20 to 30 ft. spreader is sufficiently large for this, and if short machines are used double coils may be utilized. The speed of the spreader ranges from 20 to 45 yards per minute, being governed by the rate of solvent evaporation, the smoothness of the coating desired and the type of cement used. Tension must be watched carefully on the spreader to avoid shrinking the fabric too much in width even though a gain in length is obtained. The normal shrinkage in width of a 36-inch fabric is about one inch, though it can be brought down twice this if desired. Latex spreading involves not only the shrinkage due to tension but that resulting from wetting with water. Some people claim that spreaders handling latex should be equipped with tenters to avoid excessive shrinkage.

Dry heat cures bring to the proofer a whole series of problems such as temperature variation, bar marks, discoloration at top and bottom of festoons, festoon marks due to touching or kissing, etc. These are more or less interrelated though dependent on the type of material being cured. We have found that heating coils on the sidewalls of the heater provide more uniform temperatures than if all or part of the heat emanates from floor coils. By this latter method variations as great as 20 or 30 degrees have been found in large ovens, whereas the sidewall arrangement reduced the variation in the same heaters to 5 degrees or less. Uniform temperatures are essential to good products and help to provide freedom from bloom, reversion, discoloration and other curing ailments. Bar marking is always present in dry heat cured goods and is sometimes reduced in intensity by using large diameter bars, 2 inches to 4 inches, instead of ¾-inch pipes. If leatherette festoons touch each other, the brightly glazed surfaces stick to a greater or less degree and a surface blemish results. When the cures are right dry heat provides good results, but the chance for their not being right is greater than in any other type of curing used with rubber. Accelerators having a long curing range are desirable providing they will operate at temperatures of 240° F. as well as at 260° F. Anti-oxidants are also desirable adjuncts to assist in offsetting any effect of cure and oxidation during cure, though the most effective ones darken light colored rubber subsequently exposed to sunlight.

We have mentioned above the matter of proper crown of calender rolls for providing a good surface and this factor is of still more importance in connection with making double calendered (both sides) rubberized fabrics. The running of double coated fabrics on the calender requires a great deal of skill on the part of the operator and a well adjusted machine.

First of all the fabric must be free of knots, misweaves or other heavy spots. When the first coat of rubber is applied the film is very thin, under which conditions there is little cushioning effect and the thick places may be crushed or cut. When the second side is calendered there is a great tendency for the fabric to wrinkle, cut or coat unevenly unless the roll crown is especially adjusted for this type of work. If the crown is not great enough the finished material will be heavy in the center and light toward the edges; if it is too great, the material may cut in the center. The rolls must be crowned to some degree to compensate for the spring of the rolls under operating pressure; perfectly straight rolls would actually spring or bow to the extent of several thousandths of an inch. The matter of dusting or otherwise removing the tack from the rubber on the first coat is a matter of concern to the proofer for he must take care not to get any of the tack removing material on the spread coated back of the fabric lest he later should get no anchorage when the second side was coated. Calendering generally requires much skill to produce fine fabrics, but double calendering requires unusual experience and skill.

Development of Rubber Industry

Compared to textiles, rubber is a mere stripling in the society of industries, but certain signs indicate its coming of age. Certainly the rubber industry is one of the largest in dollar volume of products. Rubber was not known to civilization till the 16th century when it was found by the Spanish explorers of South America. For 200 years little was heard of it, but in 1770 Priestly named it for us when he found it would erase or rub out pencil marks. In 1823 McIntosh founded the proofing industry by sticking two fabrics together for double texture raincoats. In 1830 or thereabouts Hancock worked out the empirical formula for rubber $C_{10}H_{16}$ and in 1839 Goodyear gave us vulcanization. The rubber industry can be dated from 1839.

On the other hand, textiles reach back to antiquity and doubtless the first weaver had very long hair and carried a club. Perhaps this long-haired gentleman was also the

first colorist of fabric. We know that indigo was described in Sanskrit and used to dye the clothes of early Egyptians as we find such fabric on the mummies. Fibers and dyes have been synthesized commercially, making the textile industry less dependent upon Nature than the rubber industry. Many attempts have been made to synthesize rubber, one of them by no less a person than Sir William H. Perkins, the eminent pioneer of synthetic dyes. He had as many as 30 chemists working on the problem at one time, but abandoned the enterprise as the price of rubber fell. This seems to be the case with later attempts at making a synthetic rubber; they were carried on vigorously when rubber was high and abandoned when the price dropped. In 1913 Dr. Wolfgang Von Ostwald lectured in this country and made the following pertinent remark: "Interest in synthetic rubber has recently subsided because of the great fall in the price of the natural product. This defection is, I think, not merited. Interest in artificial rubber should not center on the possibility of finding a substitute for the natural product but more in the possibility of making a decidedly better one. By the synthesis of a 'noble rubber' materials might be produced which would not only show properties superior to the ordinary natural article, but of a marketable character." This comment is significant when applied to DuPrene.

Most attempts to synthesize rubber arrived at the duplication of Isoprene. If successful that would produce merely a rubber-like product. DuPrene is more than this, having not only many rubber properties but many which rubber does not possess. It therefore may be economical even in the face of 3-cent rubber for such uses for which rubber is not suitable or is inadequate. DuPrene is made essentially from coal, limestone and salt. The acetylene is polymerized to monovinylacetylene and treated with HCl to form chlorobutadiene or chloroprene. Chloroprene differs from isoprene merely by the substitution of the chlorine atom for a methyl group. It is this chlorine atom which largely provides the remarkable difference. DuPrene, itself, is the result of the polymerization of chloroprene controlled by means of a small amount of Neozone D which is chemically phenyl-beta-naphthylamine. Until recently we had thought that certain antioxidants, Neozone D in particular, had little effect on DuPrene except for retarding polymerization but we now know they are effective in increasing the aging and heat resistance of DuPrene. A stock containing 2% Neozone D was in excellent condition after 160 days in the oxygen bomb whereas the stock not containing the Neozone D failed in about 70 days. This same stock also lasted 12 days in the air oven at 250° F. against 4 days for the control. The rubber chemists especially will appreciate that no rubber could be expected to approach this.

Zinc Oxide and Magnesium Oxide are essential for cure, in addition to which it is desirable to use rosin. Sulfur is not essential but is effective in speeding up the rate of cure. Brown sub, cumar, cottonseed oil, mineral oil and such materials are useful softeners. The usual fillers can, of course, be used. DuPrene stocks mix as easily as rubber and cure similarly. It is interesting to note that overcure is desirable rather than harmful. By overcure we mean longer cure than is necessary to reach the maximum physical properties. Undercures tend to result in excessive hardening of the stocks in aging, whereas longer cures do not. In the true sense of the word, it is practically impossible to overcure DuPrene. This is one indication of its heat resistance.

DuPrene stocks are resistant to oils, solvents, acids, heat and other influences which deteriorate rubber rapidly. Although some oils and solvents swell DuPrene appreciably, they do not cause it to get tender and slough off as rubber does. In 50% boiling sulfuric acid at 293° F. a DuPrene stock became slightly charred on the surface in 4 days, though the material was relatively unaffected beneath the surface. After 8 days in 50% sulfuric acid at room temperature the DuPrene was not noticeably affected.

Copper and manganese are detrimental to DuPrene as well as to rubber. A stock that normally aged for 70 days in the bomb failed in about 30 days when 1% copper or manganese as oleates were added. This is a large amount, of course, indicating again the superiority of DuPrene over rubber.

DuPrene forms cements readily in aromatic solvents and spreads easily on the fabric. The film is definitely less tacky than rubber, which is an advantage for some uses. The permeability of a DuPrene-ized fabric to hydrogen is about ¼ as great as that of a similar rubber-coated fabric. This, of course, suggests its practicability for use in balloon cloth. Other products of interest to the proofer for which DuPrene may be satisfactory and economical are printers' blankets, industrial aprons, institutional and hospital sheeting, shower curtains, oil pump diaphragms, etc. The textile trade may be interested in tension or spinning rolls covered with DuPrene cots instead of the leather, cork or other material now used. Several manufacturers are now working on this development. I understand there are some 40 million of these rolls in use and that they need frequent recovering because of oil deteriorating the covers.

DuPrene latex may sometime be available for impregnation work. It is analogous to vulcanized latex in that the DuPrene in the emulsion is completely polymerized. Samples of DuPrene and Rubber Latex are shown.

You may be interested in examining later the various samples of DuPrene and rubber products I have brought. They represent an assortment of some of the proofers' problems.

Discussion

Mr. Glancy: We have recently found that at least one textile mill will not supply us with dyed fabrics with a

copper and manganese content as low as that specified in the specification you referred to.

Mr. Byam: Our (Du Pont) purchasing department has advised me that they have had little difficulty buying raincoat fabrics meeting the copper and manganese specification and our laboratory control tests have indicated very satisfactory performance by the textile suppliers. Probably there are exceptions to this good performance in the case of special fabrics. I worked with the textile committee when the specification was formulated, at which time there was a feeling it would be impossible to obtain all colors on a low copper basis. In some cases it was impossible because the dyestuffs actually required copper to produce the desired shade and we then had to compromise by selecting a similar color though slightly different shade which could be produced with not over .002% copper. There have probably been many cases of such compromise. I suppose .003% copper can be permitted in many rubberized fabrics without serious harm for certainly the quality of rubber has been improved greatly. My point is, however, that even if we do increase the life of the rubber through the use of modern accelerators and anti-oxidants we are not offsetting the harmful effect of copper and manganese. How much copper we can afford to permit without disastrous results to our product is another matter and certainly is a problem the individual manufacturer must decide for himself. I definitely believe the textile industry should aim at the specification limit of .002% or less.

Mr. Nutting: That brings us right back to 3 or 4 years ago when Mr. Byam and I had the pleasure of being associated on a joint committee for the purpose of investigating this question of metals on fabrics intended for rubberizing. In view of the work done at that time, the results that we have had with the procedure that we developed lead me to think that our groups should get more closely together particularly with reference to the specifications of copper. I have encountered a situation in my own experience where a fabric that was turned out on the basis of a specification of .005% of copper has been perfectly acceptable to the consumer of the fabric when our own methods showed it to have .007%. Now, the question naturally arises, "Is the rubberizer working with a procedure that gives him the true content of copper in that fabric or is he finding only .002% out of a .007% content and kidding himself that he really requires a minimum of .002% to work properly?"

Mr. Byam: That is a good point and one the proofing committee discussed some years ago when the specification was written. We may be kidding ourselves somewhat as Mr. Nutting suggests. Perhaps when we say that .007 or .008% copper is alarmingly high we are not referring to the actual copper present. However, if we work from a given method of testing for copper and agree that it gives uniform results in the hands of a competent analyst and find that .007 or .008% copper by that method is definitely harmful to our product, I can't see that it makes much difference if the true amount of copper is more or less than that indicated. If on a given method of testing we know that we can accept fabrics safely having .002% or even .003% copper we can control our product properly. As far as methods of testing are concerned all we need is a good testing procedure which will be accepted and used by both textile supplier and proofing consumer.

I dare say no proofer has gone into this matter deeply enough to know how much actual copper may be permitted with safety. We think of the quantity in terms of percentage on the weight of the fabric. Obviously, there is a greater weight of copper present in a given percentage on a 20-oz. fabric than on a typical 4 or 5-oz. raincoat fabric. Are we, then, concerned with weight or percentage? I don't think the rubberizers have gone far enough into this question and no doubt they should investigate further. However, the question cannot be answered easily for we must consider the location of copper in a fabric. In a heavy fabric, a great deal of the copper present may not be in contact with the rubber film—unless the fabric is saturated or impregnated—whereas in a thin fabric nearly all of the copper is in intimate contact with the rubber. To be harmful, the copper must be in contact with the rubber in the presence of air. I think the work done a few years ago provided an excellent starting point for completely settling this problem and I trust that these two industries will continue to cooperate in the matter. For the present .002% copper on the weight of the fabric determined colorimetrically by the ferro-cyanide method seems to be safe for the proofers, though I am sure they would feel better if there was a less amount likely to be present.

MAY MEETING, NORTHERN NEW ENGLAND SECTION

THE regular bi-monthly meeting of the Northern New England Section was held Saturday, May 13th at 6:30 P. M. at Riverbank Court, Cambridge, Mass. Preceding the meeting Professor O. W. Pineo of M. I. T. demonstrated the new Model of Professor Hardy's electro-photometric color comparator in the Institute laboratory and following the regular dinner gave an informal explanation of the design and workings of the comparator as related to color matching.

Mr. N. D. Harvey of the Carbide and Carbon Chemical Corp. read a paper dealing with some recently developed synthetic esters of the glycols that are showing some very interesting properties when used as stock lubricants. Considerable interest and discussion were aroused by both subjects among the forty who were present.

Respectfully submitted.

CLARENCE L. NUTTING, *Secretary*.

SEPTEMBER 8 AND 9

Annual Convention...

American Association of Textile Chemists and Colorists in

Chicago

COMMITTEES

Technical Papers
Gordon M. Markle

Entertainment
Elmer F. Smith

Reception
A. J. Feit

Publicity
A. T. Brainerd, E. A. Johnson

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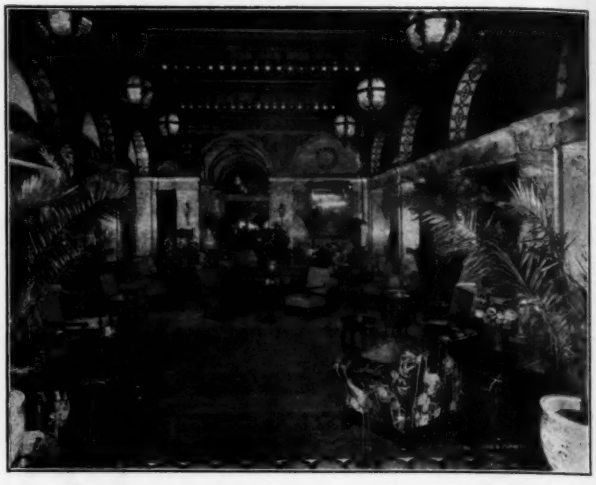

THE admission price to the grounds of Chicago's 1933 World's Fair will be fifty cents for adults and twenty-five cents for children. It will admit you without further charge to twenty-five buildings and if you go nowhere else on the grounds but to one of them, the Hall of Science, your journey will be justified. "Show it in action" is the keynote. The static or "still" exhibits of former expositions have little space here. The problem the scientists have faced is that of exhibiting everything possible in action and in moving displays that are understandable by visitors without scientific training.

In the Biology Section cell activities are demonstrated by models. The complete story of the development of organized life from the cell is seen in action. Plant growth will be shown by one of the most remarkable moving models ever created. A section of a basswood branch magnified to seven and one-half in diameter, representing a branch three years old, adds a year's growth in seventy-five seconds, becoming nine feet in diameter by the accretion of new material. In the same section are the bathysphere of Dr. William Beebe's descent 2,200 feet into the sea, and its companion miracle of applied science, Dr. August Piccard's globe in which he ascended 54,000 feet into the stratosphere.

In the Medicine Section is the Transparent Man, a figure of heroic size, the work of years by German physiologists. In this figure the illuminated tissues show all the deep organs at work, heart, lungs, circulation, digestive and nerve systems.

When you have seen how the combination of certain elements produces the result of electric refrigeration that will be a mystery to you no longer. Wireless telephoning will be simple to understand when you have seen every detail of how it is done. A huge vacuum tube in operation, changing the electric impulses that pass through it will show better than a hundred lectures how radio waves are changed and amplified.

Chemical changes will be shown as the basis of transformations of raw materials, coal, oil, wood and minerals creating products in metals, paints, dyes, soaps, medicines, lubricants, foods, inks, glass and textiles.

The science exhibits are the groundwork of the industrial food, housing, manufacturing, transportation, social science and other exhibits, in other buildings without extra charge, which show the application of science in daily life. You see this application in the Agricultural Building, Communication and Radio Building, Electrical Building, Travel and Transport Building and others.

This is just a part of the fascinating educational exhibits which you may not be able to see in a day but which are nevertheless included in the general admission of fifty cents.

The amusement and entertainment features are incredibly numerous. There will be over one hundred restaurants and sixty concessions ranging from ten to fifty cents. Go in the morning and stay until late at night, it will cost little and give you something to think about and talk about for the rest of your life. You have been told how accessible the Fair is from downtown Chicago and The Congress Hotel. If you have a free day and fifty cents you'll see more and learn more than in any other one day of your life. Don't miss it. Bring the family. Remember twenty-five buildings are included in the general admission of fifty cents, a twenty-five million dollar show that won't come again for at least a hundred years.

Below and Upper Right Corner
Interior Views of the Congress Hotel, Headquarters for the A. A. T. C. C., September 8th and 9th.

Proceedings of the American Association of Textile Chemists and Colorists

Lacquer and Its Uses*

By **E. M. HAYDEN**
Technical Director, Stanley Chemical Co.

IT has been suggested by the committee that in addition to discussing nitrocellulose lacquers in relation to rubber that some mention be made of its uses in other fields. Oftentimes one industry can utilize materials and processes of other industries which are in no way related. Lacquers find extensive use in fields which are most unrelated and it is hoped that by mentioning some of these uses some new ideas may be germinated.

The so-called metal and wood industries are two of the largest consumers of nitrocellulose lacquers, and their demands have brought about the creation of many special purpose lacquers. Some instances might be mentioned of interest. The demands of the washing machine manufacturer for example have brought forth lacquers which will withstand the destructive action of household washing soaps when ordinary lacquers would discolor and come off under this ordeal. The makers of metal buttons have demanded and received lacquer finishes which will withstand the rough treatment of laundry solutions and pressing machines. Lacquers not especially formulated for this purpose would disappear on the first trip to the laundry.

An interesting application of lacquer from a decorative standpoint is its use on vanity and cigarette cases to replace vitreous or cloisonet enamel. These cases are sprayed with two or more coats of a hard, colored lacquer and after allowing to dry, the lacquer surface is buffed to a mirror-like finish. Decorations in many colors such as flowers are often put on these articles by spraying the colors through a series of stencils and the results of this stencil work are often difficult to distinguish from hand painting. When such designs are used, they are covered with a coat of clear lacquer before buffing. The advantages of a buffed lacquer finish over vitreous enamel are in speed of application and in elimination of high temperature baking. The lacquer finish will also withstand blows which would shatter the brittle vitreous enamel.

One of the oldest uses of lacquer on metal is that of transparent lacquer on polished metal surfaces to prevent tarnishing. In spite of the fact that clear lacquers have been used for this purpose for a great many years, there had been little improvement in these lacquers until a few years ago. The old lacquers would go to pieces in no time when exposed to the sun and elements, and much trouble was experienced with them in connection with plated metals by the appearance of annoying spots. Recent developments have brought forth clear metal lacquers that will stand up out of doors for a long time and the old spotting trouble has been largely eliminated. The largest users of clear metal lacquers are the hardware and electrical fixture manufacturers.

The type of lacquer used on wood is quite different from metal lacquer. A metal surface is generally smooth and the thin film produced by a lacquer of relatively low solid content is therefore entirely satisfactory. A wood surface requires a lacquer of high residual solid content to fill the roughness of the wood and thereby give a smooth finish. Also in the case of transparent wood lacquers a relatively thick film is necessary to give the appearance of depth to the finish. On the other hand the metallic surface offers many problems of adhesion and the lacquer must be compounded to take care of this, while the wood surface offers mechanical adhesion by the fibrous nature of its surface. While much wood lacquer is rubbed to a semi-dull finish, a large portion of it is produced by the use of a semi-dull lacquer. By incorporating materials such as aluminum or zinc stearate in a lacquer, such finishes without rubbing resemble closely the hand rubbed finishes. In addition to speed of application, wood lacquers offer the advantages of excellent durability and appearance, and incidentally one need never fear of sticking to a lacquered chair on a hot day as has happened often with a varnish finish.

Before discussing flexible lacquers for use on rubber, it may be interesting to mention a few uses of which those not entirely familiar with lacquer applications may not be aware. The latest lacquer use which many laboratories are working on is the development of clear and colored lacquers which must be alcohol resistant for use on bars, trays and even beer mugs. Here are a few

*Presented at meeting, N. N. E. Section, April 6th.

more examples. A good percentage of the fishline made in this country is coated or impregnated with flexible lacquers to waterproof and weight it. Fingernail polishes are transparent lacquers. A good portion of women's shoes made today have the soles cemented on with a clear lacquer which besides making the process very rapid, eliminates nails and stitching. Fiber rugs are decorated with colored lacquers.

True nitrocellulose lacquers have their limitations and depend on modification to obtain special properties. Just so there is no misunderstanding of what we mean by a lacquer, we will briefly describe the general classes of ingredients which go to form a lacquer.

Lacquer Ingredients

There are four main ingredients in a clear lacquer. A pigmented or colored lacquer is merely a clear lacquer into which a color has been incorporated. The four ingredients are nitrated cotton or nitrocellulose, plasticizer, resins and the solvents in which the first three are dissolved. You can readily see that with a lacquer having in the case of a clear lacquer, four main ingredients namely, nitrocellulose, plasticizer, resins and solvents, you can form innumerable varieties by changing any one of these ingredients.

The two ingredients which give the necessary flexibility and adhesion to rubber are the plasticizer and the resin. A plasticizer is a material which imparts flexibility to the lacquer film, such as castor oil, di-butyl phthalate and many others. A resin may be a natural or a synthetic gum. It is incorporated into the lacquer to produce proper adhesion to various surfaces, to give gloss or resistance to various things such as alkali, acids or alcohol.

Many of us think of a resin as something which is hard and quite brittle. As a matter of fact, particularly in the case of the synthetic resins, there are a great many of them which are extremely flexible and some so much so that they actually take the place in a lacquer of not only the resin, but also the plasticizer. In other words, you can perform the two duties by the use of one material.

The most interesting modifications of nitrocellulose lacquers are obtained by the use of synthetic resins, because the resins themselves can be modified in so many ways. The resin manufacturers are constantly thinking up new things to mix together, and lacquer chemists are kept busy finding uses for them. With the large variety of such resins and their modifications at hand, there becomes almost an infinite variety of possible modifications of a nitrocellulose lacquer. For this reason competitors in the lacquer industry often do not attempt to duplicate each other's products by strict analysis of the ingredients. Rather, duplication is attained by aiming at a result through the use of one's own ideas on formulation. As a result the new lacquer oftentimes turns out to be even superior, and this promotes a healthy condition of progress in competing research laboratories.

Just a word as to what synthetic resins are. These may be a natural resin modified by chemical reaction—the one most widely used is so-called "ester gum," which is rosin esterified with glycerine. The newest and some of the best known types are the bakelite and glyptal resins. The bakelite type is a phenol formaldehyde resin, while the glyptal type is a phthalic anhydride glycerine condensation type. Both of these resins are modified in all kinds of ways to produce varying results. They are usually modified during the manufacturing process of the resin itself. To explain this a little further let us take a glyptal resin to see how it may be modified. Let us assume that you start out with glycerine and phthalic anhydride, altho you can use many anhydrides in place of the phthalate. During the reaction you may add, in order to make the resin more flexible, the free fatty acids of some oil, let us say of linseed. If you however use the same formula, but use the free fatty acids of china wood oil, you will produce a resin of different characteristics and behavior.

Nitrocellulose itself gives a film which has excellent tensile strength and seems unusually hard and tough. By itself, however, a very poor film is formed which has poor adhesion to many surfaces. For use on cloth the most necessary modification is of course to impart flexibility to the film.

Lacquering Rubber

Now when lacquering rubber there are two very necessary modifications and these are flexibility and adhesion. Flexibility must be obtained with as little alteration to the film as possible and must be as permanent as possible. Plasticizers for nitrocellulose generally take the form of non-volatile liquids and it is quite natural to expect that they would lessen the tensile strength and tend to make the film sticky if used in excess. For many purposes where cheapness is more essential than other properties, pure castor oil is satisfactory. However, castor oil has one very undesirable property and that is of leaving or sweating out of the lacquer film when subjected to heat. The film which remains will eventually become brittle and "boardy." As an example of this, if a waterproof coating of lacquer plasticized with pure castor oil were applied to cloth and the cloth subsequently made into curtains, these curtains would stiffen up if hung for any length of time over a radiator or were washed a number of times in really hot water. In this case, the oil comes to the surface and can be rubbed off. In the case of lacquers for use on rubber if castor oil is used as a plasticizer, instead of coming to the surface it will in many cases soak into the rubber. This action in addition to making the lacquer film brittle, will cause over-softening or rotting of the rubber.

Fortunately there are a great many other plasticizers that can be used to make nitrocellulose flexible and many

of these do not migrate from the film of lacquer. The worst shortcoming of the average plasticizer is that it causes over-softening of the film or to put it in another way, it causes the film to have very poor tensile strength. However, lacquers can be made which will give a good, dry, light resisting and tough film. These improved lacquers have already been applied to a great many types of fabrics and rubber coated articles and doubtless just as in the past few years there have been major improvements in this field, there will be further steps in the next few years to improve the finish still more.

The application of nitrocellulose lacquers to rubber surfaces is probably one of the most difficult with which the lacquer manufacturer has had to contend. It was early found that the *composition*, the *type of cure* and the *type of finish* of the rubber all played an important part in formulating a lacquer which would stick to that particular article made of rubber. In other words not only the general composition of the rubber itself but whether it was subjected to *dry heat, ammonia, sulfur chloride*, or some other type of cure, played a deciding part on whether the lacquer coating was satisfactory or not. All of these form a *rubber surface* which seems to have different reactions toward lacquer coating.

The treatment of the cured rubber surface has a definite effect on lacquers. In other words, the various types of materials used to dust the rubber, the matter of the use of water shellac, all have effects on the adhesion or non-adhesion of a lacquer film. In fact we have seen lacquers which adhered perfectly to a rubber coating of a definite composition lose entirely its adhesion or durability by the change of only one or two items in the rubber formula. Some of the things which have great effect on the adhesion and durability of a lacquer film are the accelerators and anti-oxidants.

The use of nitrocellulose lacquer on rubber is probably one of its few uses where rapid drying is not its most interesting property. To be sure, the rapid drying feature is often helpful in application, but it becomes secondary in many cases because often the lacquer is applied prior to vulcanization, and the baking action of vulcanization doubtless takes care of a slower drying material.

The nature of the finish obtained with lacquer on a rubber surface is its most interesting feature. This finish is dryer and harder than can be obtained any other way with the exception of bromine, and is of course without the hazard and uncertainty of a bromine finish.

In many cases rubber is made to look like leather, but no matter how close the appearance approaches leather, the surface will still feel rubbery and perhaps sticky. A coating of a proper lacquer will entirely remove the rubbery feel and give a dry, leathery feel. In addition a lacquer finish allows a wide range of gloss effects from a dull calfskin to a bright lizard shine. One other point in favor of lacquer coating on rubber is the fact that the lacquer coating protects the rubber, not only from the atmosphere, but from oil and grease.

There are two types of lacquer finish for rubber which are in use with equal satisfaction. One is the *continuous film*, the other the *discontinuous film*.

The continuous film variety must necessarily include all clear lacquers because any break in a clear lacquer film would be very noticeable. The continuous film lacquers are not quite as dry to touch as the other type because they are naturally more flexible. Some of the continuous film clear lacquers will stand an appreciable stretch without any noticeable break even under a microscope. They can be applied either before or after vulcanizing.

Discontinuous film lacquers are confined to pigmented lacquers and are designed to be used where an exceedingly dry surface is sought. They are usually applied before vulcanization and give a film which is cracked so finely that the cracks are scarcely visible. It is absolutely necessary that this type of lacquer have excellent adhesion because otherwise the fine cracks would be a starting place for peeling. The thickness of the lacquer coating is important. The best results seem to be secured with a thin film. This is particularly true of the discontinuous type of coating.

Where adhesion is of prime importance a lacquer designed to be applied before vulcanization will give the best results. In the first place the uncured rubber surface gives the lacquer more of a chance to grab ahold than a cured surface. Also the baking obtained in the cure improves the bond greatly. Clear and colored lacquers change color sometimes when applied to rubber. This is particularly true of lacquer coatings applied before cure.

The high temperature of a dry heat cure will turn a clear lacquer yellow in color. Pigmented lacquers under the same treatment tend toward a yellowish cast while some pigments as you know will change color appreciably not only due to the temperature but also because of reaction with sulfur or some other ingredient of the rubber compound.

Clear lacquer applied after cure to rubber articles may discolor on age. This can usually be corrected by changing something in the compound. Recently we found in one article that reducing free sulfur to the minimum after vulcanization stopped the discoloration of this particular clear lacquer.

There are of course cases, such as in molded goods, where lacquer must be applied after vulcanization. In these cases it is quite often possible to increase adhesion by sacrificing a small amount of flexibility and many molded articles are being finished satisfactorily with lacquer. In some cases a lacquer applied to a molded article after cure can have the adhesion noticeably improved by giving the article a low temperature bake.

There is one place where to the best of our knowledge lacquers have failed to work, and that is attempting to

lacquer before cure, and then curing by the *ammonia* process.

The application of lacquer to rubber surfaces follows the usual methods. For rubber coated cloth either the spreader, varnish knife, off-set roller or spray methods have been used successfully. For molded or formed articles such as balls, overshoes and electrical parts either spray or dip methods work well.

It might be well to mention a few rubber articles that are being lacquered successfully:—rubber coated cloth, rubber coated shoe lining, rubber overshoes, inflated and sponge rubber balls, golf balls, molded parts for electrical appliances, rubber dolls, rubber tile.

We may expect rapid strides in the coming years in the lacquering or finishing of rubber articles. There are many enamels now made containing no nitrocellulose, depending on a synthetic resin to do the duty of both the nitrocellulose and resin in the enamel. These are the so-called synthetic enamels. They have certain advantages and certain disadvantages over lacquer enamels.

Some of the advantages are lower cost per square foot of surface covered, cheaper solvents for thinning, and in certain cases marked resistance to certain alkalis and solvents.

The disadvantages to date are that they dry much slower than lacquer enamels, they lack real flexibility, and some types require baking in order to produce a hard, dry surface.

However, we believe that eventually you will see synthetic finishes which will be used to finish flexible rubber articles.

UNEMPLOYMENT REGISTER

(See notice on page (209) 357)

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive

A-1

Education—Ph.B., Brown Univ. '27, P.G. at N. C. State (M.S. this June).

Experience—several years experience as an analytical and research chemist; private research work on sulfonated oils. Twenty-seven years old, married. Will supply references.

A-B-1

Experience—over twenty years' experience in the laboratories of various chemical manufacturers, four months' experience as second hand in dye house, familiar with all types of dyes and fibers. Thirty-nine years old. Will supply references.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

B-1

Education—educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following; celanese, rayon, cotton backs, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-4

Experience—Overseer of cotton and rayon piece dyeing. Familiar with all machines and all classes of colors. Has knowledge of chemistry, was at one time demonstrator of chemistry and dyeing at Manchester (Eng.) Institute of Technology. Prefers N. E., N. Y., N. J., or Penn., but will go anywhere. Fifty-two years of age.

B-5

Experience—Nine years of yarn dyeing on rayon, silk, cotton, and novelty yarns with acid, direct, vat and naphthol colors. Experience in yarn printing, fastness tests and also on dyeing silk piece goods and rayon knit goods. Will go anywhere; references.

D-1

Education—Graduate textile course, 1911, Georgia School of Tech.

Experience—Has had experience in all branches of the textile industry but chiefly in sales work. Was at one time in the dyestuff business and later in hosiery manufacturing. Prefers Middle Atlantic or southern states.

F-1

Education—Textile Institute, Alexander Hamilton Inst., Extension work at Brown Univ., working knowledge of German.

Experience—Has had executive departmental work with all types of textiles manufacturers. Acquainted with all types of textile machinery, dyestuff application, laboratory practice, cost methods, and checking methods and processes. References.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

AMERICAN
DYESTUFF
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"BUSIER MILLS"

UNDER the above caption, the New York *Sun* of May 22nd comments editorially upon the current increased activity in textile lines. It is interesting to note that the member of the *Sun's* editorial staff responsible for the article is a former managing editor of the REPORTER who forsook us for broader fields. The editorial in question follows:

"Perhaps the first high wave of business recovery will come in cotton sheets, silk lingerie and other products of American textile mills. There is a strong seasonal influence, of course, in the current rebound of the industry, but the recent history of the cotton and woolen trades gives some hope that the latest activity is a genuine comeback. It is not so sudden as it may appear. Signs of improvement in textiles were almost sure to come with spring this year, for the basic strength of the industry has repeatedly drawn forth the assurances of its leaders in the last two years.

"'We are now proceeding to a greater and better business era in textiles than we have ever known before.' These words were spoken in May, 1931, by a textile executive addressing a meeting of the New York Board of Trade. Such enthusiasm seemed premature, however, when the upturn which marked the late summer of 1931 failed to revitalize a substantial part of the industry outside New England. On the threshold of 1932 the manufacturers again heard predictions of busier days. The cotton industry was organized to push the buying of its fabrics for a variety of new uses. In New England the mills talked of adjusting their output to heavier demands, though they moved with caution. Then, last summer and fall, came a wave of buying heavier than any the industry had experienced since 1929.

"A simple comparison will show how deep was the valley into which the textile business had apparently settled. In 1929 the industry employed 1,707,000; by the end of 1931 the number had declined 20 per cent. In 1929 the value of the industry's products was $9,243,302,500; by the beginning of last year it had fallen 37 per cent. Depressed prices forced down the valuation, however, hence the actual volume of business was not quite so bad as the figures show.

"What cheered the textile manufacturers as 1933 dawned was the report of low stocks on hand in wholesale and retail markets. The National City Bank letter for January said: 'Activity has been better sustained in the textile mills than elsewhere, and of all the industries only in textiles and shoes were factory operations toward the close of the year (1932) greater than one year ago.' Less than two months later, in the last week of February, it was said that the first favorable news would help create a demand for all types of goods to fill empty shelves. The spurt last summer had indicated how strong the buying might become, for in September the cotton mills were operating at 72 per cent of their capacity.

"Several mills in Fall River reopened in March, and after the bank holiday orders were resumed in some parts of New England. Last week cotton mill activity was at the highest rate in several years. Jobbers, chain stores, retailers are reported as 'clamoring for goods.' A large woolen mill in New Hampshire has increased its pay rolls. One of the biggest cotton mills in the country has raised wages 15 per cent. Several mills in Alabama have been operating at full capacity with a higher wage scale. Business has not been confined wholly to domestic orders, for a review of 1932 trade shows increases in exports of cotton yarn and fabrics, the volume of yarn alone rising a million pounds over 1931 exports. The first signs of stronger buying power on the public's part will give further assurance that the hopes of the textile industry are not unfounded."

Dr. Rose Lectures To Students

Dr. R. E. Rose who was the principal speaker at the meeting of the American Association of Textile Chemists and Colorists held in Greensboro, May 13, visited the Textile School of North Carolina State College on his way back to Wilmington, Delaware. While at the School he gave a very interesting and instructive talk to the students.

Other recent visitors to the School were: Mr. Harold Faust, Laboratory Manager of The Ciba Company, Greensboro, who lectured and demonstrated the dyeing of vat colors on cotton yarn, and which also covered color matching, money value and nomenclature; Mr. E. P. Davidson, Manager of the Charlotte Laboratory of the du Pont Company, who discussed the subject of "Sulphonated Fatty Alcohols."

RAYON DYEING AND FINISHING

(Continued from page 354)

At first thought it would appear that such a procedure would completely ruin the fabric processed. As a matter of fact many thousands of pounds have been successfully processed in this manner and have given complete satisfaction. The "joker" in the process is the use of equal quantities of soda ash and sodium-hypo-chlorite solution. A formula for the production of a three-quarter bleach in the scouring bath follows. It should be understood that this formula is not recommended by the writer.

Typical Scouring and Bleaching Procedure

(*Highly dangerous though successfully used.*)

Per 100 Pounds

(1) Fill machine with water.
(2) Load with fabric.
(3) Add 2 lbs. Soda Ash.
(4) Turn on steam and run goods for 10 minutes.
(5) Add 5 lbs. Soap.
(6) Add 2 lbs. "Soluble Pine Oil" or similar solvent containing material.
(7) Raise bath to boil. Observe condition of dye bath at all times. If bath does not show a good, clean, sudsy condition, add more soda, soap, and pine oil.
(8) Run at boil 15 minutes.
(9) Shut off steam and run 10 minutes.
(10) Add 5 lbs. Soda Ash.
(11) Add 8 lbs. Sodium-hypo-chlorite solution containing 14 per cent available chlorine. Add bleach solution slowly—feed it into front of machine during five minutes.
(12) Run twenty minutes in bleach liquor.
(13) Drop bath.*
(14) Fill machine and proceed with dyeing operation.

*If hard water must be contended with drop only about four-fifths of liquor. Fill machine immediately with *hot* water, pouring the soap or soluble oil used in the dyeing process, together with the soda ash or tri-sodium-phosphate, into the incoming stream of water.

The above described bleaching procedure is much more mild in its action on circular knit rayon fabric than one unfamiliar with the process would suppose. The alkalinity of the bath retards the bleaching action and prevents the chlorine from excessive action on the fabric.

Most of the available chlorine has been used up at the end of the twenty-minute bleaching period. The slight traces remaining in the fabric are dispersed throughout the dye bath and are completely destroyed by the boiling bath during the dyeing operation.

The following procedure is typical of the various procedures that are today used in many dye houses for the production of three-quarter bleach as a base for bright shades. It is possible to reduce the time of treatment indicated below by increasing the temperature or strength of hypo-chlorite or by reducing or omitting the anti-chlor treatment. Each of these possible variations is practiced by individual mills. The procedure given below has been found to be absolutely safe and trustworthy by mills endeavoring to obtain the best possible results at the minimum risk of tendered fabric.

Procedure for Production of Three-Quarter Bleach Per 100 Pounds

1. Scour as usual.
2. Drop bath.
3. Fill machine with fresh cold water.
4. Add 8 lbs. sodium-hypo-chlorite solution (12-14 per cent available chlorine).
5. Run goods 20 to 35 minutes, the time depending upon the degree of bleaching required and the appearance of the fabric as judged by the dyer.
6. Drop bath.
7. Run in fresh liquor.
8. Add 1 lb. anhydrous sodium bi-sulfite powder.
9. Run goods 20 minutes.
10. Drop bath.
11. Proceed with dyeing operation.

Although the two above given bleaching procedures, and many variations of the same, are successfully used for the production of three-quarter bleach effects as a ground for light bright shades, they will not produce the so-called "Bleached White" effect. A more lengthy and more drastic treatment is necessary to satisfy the current trade demand for "Bleached White" fabric. The following procedure, though lengthy, has been successfully used for a long period of time (as time goes in the rayon industry) without complaint on the part of the ultimate consumer.

Procedure for Production of Full Bleach Per 100 Pounds

1. Scour goods extra thoroughly.
2. Rinse very thoroughly to remove every trace of soap.
3. Make up fresh cold bath.
4. Add 10 lbs. sodium-hypo-chlorite.
5. Run one-half to three-quarters of an hour.
6. Drop bath.
7. Make up fresh bath.
8. Add 1 per cent sulfuric acid.
9. Run ten minutes.
10. Drop bath.
11. Make up fresh bath.
12. Add 1 lb. sodium-bi-sulfite.
13. Run ten minutes.
14. Drop bath.
15. Rinse thoroughly several times.
16. Add bluing to final rinse.
17. Extract and dry as usual.

(To be continued)

Oxycellulose and Hydrocellulose

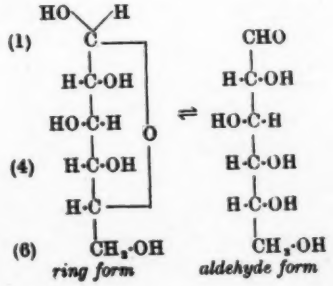
(Continued from page 356)

cellulose material than for cotton. On dyeing with sulfur dyestuffs, and also with the different classes of vat dyestuffs, the depth of shade obtained on the oxycellulose material was less, and that on the hydrocellulose material slightly less, than that on the cotton.

In order to give an explanation of the dyeing, chemical, and physical properties peculiar to the so-called oxycellulose and hydrocellulose materials, it will be necessary to consider briefly the modern conception of the constitution and conformation of cellulose, based on a definite experimental foundation[9-12], [14] corroborated by X-ray data[13] and elaborated by thorough physico-chemical investigations.

The basal unit of cellulose is the β-glucose molecule in the form of a six-membered ring; a large number of such units condensed through the operation of principal valency constitute the cellulose chain or macromolecule.

The earliest representation of glucose was a straight chain with a free aldehyde group in the end position. Glucose does not always react as though it contains a free aldehyde group, however; it is therefore considered that the following equilibrium exists under certain conditions.



It is more rational to represent the glucose molecule as a closed hexagon.[11], [10] This form is the only one the dimensions of which will give a satisfactory interpretation of *X*-ray data.[15],[13] There is much chemical evidence in favor of the view that the cellulose chain consists of such hexagonal units linked together at positions (1) and (4) by the elimination of a molecule of water between adjacent units, which are therefore linked together by a glucosidic oxygen atom. This structure was put forward by Haworth from a consideration of chemical evidence[11], [9] and also by Meyer and Mark from results obtained by *X*-ray investigations, since the dimensions of the six-membered ring glucose units linked at positions (1) and (4) are accommodated exactly by the space lattice required by *X*-ray data.

The purest and least degraded celluloses known, such as carefully scoured cotton cellulose, have low copper numbers of the order of 0.01,[17] which indicates either that the chains of glucose units are endless, or that the terminal glucose component is modified in some way, perhaps by oxidation to the acid or lactone group as suggested by Haworth and E. G. V. Percival.[18] Staudinger is of the opinion that the chains are in the form of long narrow loops or double threads which constitute the cellulose macromolecule, and are of a semi-colloidal nature. He has demonstrated many analogies between solutions of cellulose and its derivatives, and solutions of polyoxymethylenes and polystyrene.[14] Meyer and Mark consider that bundles of parallel chains of glucose units termed micelles constitute the structure of cellulose. Since the viscosity of dilute solutions of cellulose tri-acetate in tetrachloroethane, and of cotton cellulose in Schweitzer's reagent, does not vary with rise in temperature, Staudinger considers that the presence of micellar colloids is inadmissible since such bundles of chains of glucose units held together by auxiliary valency would be broken up by the rise in temperature, resulting in a lowering of viscosity. By comparing the viscosities of solutions of cellulose acetate with those of degraded cellulose acetates, and of cellulose itself with those of the dihydrates from the degraded cellulose acetates, Staudinger arrived at a molecular weight of purified cotton of about 190,000, there being over 1000 glucose units in the macromolecular chain. He therefore considers that the macromolecule of cellulose consists of an endless chain, or narrow loop, the two long sides of which are almost parallel.

Haworth is of the opinion that the chains of glucopyranose units in the cellulose constitution are not endless. He has shown that the trimethyl derivative, prepared under very mild conditions from an acetone-soluble cellulose acetate of a homogeneous nature, probably contains 100-200 methylated glucose units in a chain terminated by a tetramethylglucose group, since on hydrolysis of fully methylated cellulose, and subsequent complete methylation of the hydrolytic cleavage products to the glucosides, tetramethylmethylglucoside was obtained in an amount representing 0.6% of the total.[12] Whether this terminated chain structure is also applicable to native cellulose is a matter open to conjecture. It is certain,

however, that whether the cellulose macromolecules are in the form of endless or open chains, they contain a very large number of glucose units, and at least 100.

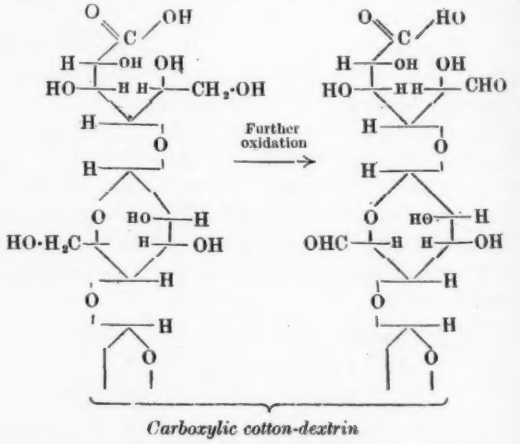
The first stages in any degradation of cellulose or its derivatives consists in the scission of the macromolecular loop or long chain, as the case may be, followed by fission into short straight chains, usually of varying lengths; the average length of the chains depends on the nature of the degradation, mild degradation resulting in comparatively long chains which would break down into shorter chains on more drastic degradation, the process being progressive.[9] It can be seen from the foregoing why in the initial stages of formation of "oxy-" and "hydro-cellulose," the products obtained are similar in properties; it will also be realized that such a procedure must of necessity give rise to a mixture of degradation products. It is the end-groups of these chains which are of primary importance in determining the properties of the degradation products, and the author considers that it is here that a difference between "oxycelluloses" and "hydrocelluloses" is to be found.

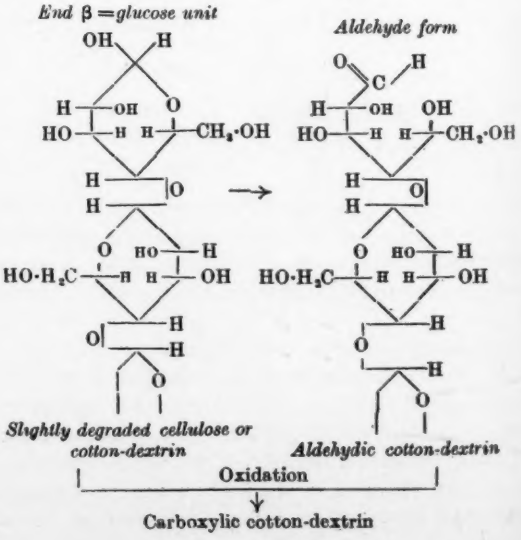
The next stage in the formation of "oxycelluloses" and "hydrocelluloses" will therefore be an attack on the end glucose units of the chain. The author considers that it is possible that in the formation of "hydrocellulose" the six-membered rings of these end units are opened out to give the active reducing aldehyde form, while in the formation of "oxycelluloses" some or all of the exposed aldehyde groups are oxidized to carboxyl groups. It is also probable that the $CH_2.OH$ group at position (6) in the glucose molecule is oxidized to an aldehyde group. Since there are several of these $CH_2.OH$ groups in the molecular chain, there is considerable opportunity for the formation of aldehyde groups. During the oxidation further "cracking" may also occur to yield shorter chains and so expose more aldehyde groups.

It is therefore considered that the material prepared in this investigation by a treatment of cotton with either sulfuric or hydrochloric acid contains free aldehyde groups in its structure and corresponds with a so-called hydrocellulose, while that prepared by a mild oxidation with hypochlorite, or permanganate, either acid or alkaline, contains both carboxyl and aldehyde groups, the carboxyl group most probably being at the terminal position in the chain of glucose units, and corresponds with a so-called "oxycellulose." The chemical, dyeing, and physical properties of these two materials examined can be interpreted by the representations given below. It is suggested that a new terminology be adopted for these degradation products of cellulose, the terms hydrocellulose and oxycellulose being replaced by others more suitable. Both products are cellodextrin derivatives of a more or less complex nature and might therefore be classified under the general term "cotton-dextrin products," which indicates the particular form of cellulose from which they are derived. "Hydrocelluloses" exhibiting the properties described above can be appropriately designated aldehydic cotton-dextrins, while "oxycelluloses" possessing the characteristics described above can be designated carboxyl cotton-dextrin-aldehydes, or more simply carboxylic cotton-dextrins. The terms aldehydic cotton-dextrin and carboxylic cotton-dextrin are sufficiently specific and convey an idea of the nature of the products. Any substances representing intermediate stages in the formation of both aldehydic and carboxylic cotton-dextrins can be referred to as cotton-dextrins and are probably present to a certain extent in both degraded forms of cotton.

The stages in the formation of aldehydic cotton-dextrin (a "hydrocellulose") and carboxylic cotton-dextrin (an "oxycellulose") may be represented by the scheme shown in the next column.

According to this scheme it should be possible to produce "oxycellulose" by means of a mild oxidation of "hydrocellulose"; this was actually accomplished by means of dilute hypochlorite solution, by ½% potassium permanganate with ½% sodium carbonate solution, and also by 1% potassium permanganate with ½% sulfuric acid solution. Cotton piece was treated in the same solution, and the metal affinity tests showed that slightly more carboxylic cotton-dextrin was formed from the aldehydic





cotton-dextrin material than from the cotton by the acid permanganate oxidation.

It is helpful to employ the proposed terms for degraded cotton products which exhibit the characteristic properties previously outlined, and the representations advanced above are in strict accordance with these properties and may therefore be reasonably adopted in the absence of any contradictory evidence. The term aldehydic cotton-dextrin will be used for the "hydrocellulose" and carboxylic cotton-dextrin for the "oxycellulose" prepared and employed in the investigation described in the experimental portion of this paper.

The scission of the macromolecular loops or of the very long chains of β-glucopyranose units to give comparatively short molecular chains, which occurs during the formation of these dextrin substances, accounts for the decrease in viscosity of their cuprammonium solutions, which can be employed as a means of estimating the extent of the degradation, and also for the loss in tensile strength manifested by the tendering of cotton on treatment with acid or with sodium hypochlorite under conditions which are too severe. However carefully the conditions of preparation of alhehydic and carboxylic cotton-dextrin are controlled, it cannot be conceived that the macromolecules will break down into molecular chains which are exactly equal in length; the final product must of necessity, therefore, be mixtures of dextrin products. The important point, however, is that in aldehydic cotton-dextrin it is considered that free aldehyde groups are present, whereas in carboxylic cotton-dextrin, carboxyl as well as aldehyde groups are exposed, whatever the length of the component molecular chains. It is the presence of these groups which makes possible selective identification tests, and accounts for the peculiar dyeing properties.

The poor affinity for direct cotton dyestuffs exhibited by carboxylic cotton-dextrin is probably due to the presence of its carboxyl groups and also to the shortness of the molecular chains.

Assuming that the dyestuff becomes ionized in the dyebath, the dye acid would have no affinity for the carboxyl group; indeed it seems reasonable to expect that the potentially electronegative carboxyl group will exert a definite repulsion to the electronegative dye acid ion and tend to keep it in its ionized state, thereby acting in opposition to the hydrogen atoms present in the cotton-dextrin molecular chain. From a chemical point of view, if a double decomposition reaction occurred between the end group of the cotton-dextrin molecule and the dyestuff, it would be expected that the sodium atom of the dyestuff would replace the hydrogen atom of the carboxyl group and the free dye acid would remain in the dyebath. In a consideration of colloid absorption it would be necessary to determine the type of charge, if any, on the cotton-dextrin—whether a positive or negative potential difference—before advancing a theory. It may be that the carboxylic cotton-dextrin carries a negative charge, just as the tannate colloid is negatively charged, and therefore would have no affinity for electronegatively charged colloid particles of dyestuff but would have an affinity for the positive color base of basic dyestuffs. Another important aspect to be considered is also the accommodation of the dyestuff molecule by the structure of the fibers. It is reasonable to consider that the endless macromolecular loops, or the long chains of glucose units clustering together in the form of a micelle, would be more accommodating in this respect than would be the short straight chains—probably removed from one another—of the carboxylic or aldehydic cotton-dextrins. Indeed, it is probably because of this accommodating effect that aldehydic cotton-dextrin has slightly less affinity for direct dyestuffs than has cotton.

Carboxylic cotton-dextrin has a greater affinity for basic dyestuffs than has cotton, since the exposed carboxyl groups will react with the positively charged base of the basic dyestuff; this effect evidently predominates over the decrease in accommodating power of the dextrin molecules. This accommodation effect, however, is most probably the reason why aldehydic cotton-dextrin was found to have slightly less affinity for basic dyestuffs than has cotton.

Mordanting with tannic acid confers affinity for basic dyestuffs when employed with cotton cellulose, since it supplies the necessary acidic groups; it does not confer a greatly increased affinity with carboxylic cotton-dextrin since acidic groups are already present; with aldehydic cotton-dextrin, however, it would again be expected that the affinity would be increased. Solid shades are therefore obtained on carboxylic cotton-dextrin, aldehydic cotton-dextrin, and cotton cellulose by first mordanting with tannic acid and fixing with tartar emetic and then dyeing with basic dyestuffs.

Dyeing with sulfur and vat dyestuffs resulted in lighter shades on carboxylic cotton-dextrin and aldehydic cotton-dextrin material than on cotton, since the reducing properties of the former two materials would nullify some of the color value; there would also be less affinity between the dyestuff molecule and the short molecular dextrin chains due to the "accommodation effect."

The enhanced affinity for salts of metals was the basis of all of the selective tests for carboxylic cotton-dextrin, and is attributable to the presence of the carboxyl group. It is quite possible that the reaction may consist in the formation of a bridge between two adjacent molecular chains of the dextrin product; thus, the reaction between carboxylic cotton-dextrin and ferrous sulfate may occur according to the scheme:

$2R.C(O).OH + FeSO^4 \rightarrow R.C(O).O.Fe.O.C(O).R + H_2SO_4$ (R representing the cellulosic residue, or remainder of the dextrin molecular chain.) The dextrin-metal complex is quite stable in water at 80° since after treatment in hot water followed by repeated rinsing and subsequent immersion in potassium ferricyanide solution, a deep blue color develops owing to the formation of "Turnbull's blue" *in situ* on the dextrin material. Evidence in support of the above representation was furnished by immersion of carboxylic cotton-dextrin material in neutral

ferrous sulfate solution, when it was found by testing with B.D.H. Universal Indicator that acidity developed within a few minutes.

EXPERIMENTAL

Preparation of carboxylic cotton-dextrin material from cotton piece

Cotton piece was immersed at 18° for 15 minutes in an aqueous solution of sodium hypochlorite (*d* 1.02), containing ½% of soda ash on the total weight of solution. The material was then squeezed between rollers and without rinsing was air-dried at room temperature during 3 hours, when it was washed in water, then in ½% aqueous sodium hydrosulfite solution at 60°, and finally in water. The white material thus obtained was fairly tender and was free from hypochlorite.

Preparation of aldehydic cotton-dextrin material

(*a*) Cotton piece was steeped in 5% hydrochloric acid for 15 minutes at 18°, then squeezed through rollers, and without rinsing was air-dried at room temperature during 3 hours, when it was progressively washed in hot water, cold 0.1% soda ash solution, and water. The white material thus obtained was fairly tender and was neutral.

(*b*) As method (*a*) but 5% sulfuric instead of 5% hydrochloric acid was employed.

The material obtained by method (*b*) had the same physical, chemical, and dyeing properties as that obtained by method (*a*).

Preparation of carboxylic cotton-dextrin material from aldehydic cotton-dextrin material by mild oxidation

(*a*) The aldehydic cotton-dextrin material was treated with an aqueous solution of sodium hypochlorite of *d* 1.02 containing ½% of soda ash on the weight of solution, at 18° for 15 minutes, when it was squeezed and without rinsing was air-dried at room temperature, washed in water, ½% aqueous sodium hydrosulfite solution, and finally well rinsed in water. The material obtained exhibited the same physical, chemical, and dyeing properties as the carboxylic cotton-dextrin material obtained directly from cotton cellulose.

(*b*) Piece of aldehydic cotton-dextrin material and normal cotton piece were treated with a solution of ½% potassium permanganate and ½% sodium carbonate at 40° for ½ hour, when they were well rinsed and steeped in dilute hydrogen peroxide until the brown potassium manganate was removed. Both materials then showed an increased affinity for methylene-blue and became colored dark blue on immersion in ferrous sulfate, rinsing, and subsequent immersion in potassium ferricyanide solution. A cotton control did not become colored.

(*c*) A treatment similar to (*b*) with the exception that a 1% potassium permanganate and ½% sulfuric acid solution was employed. Both materials had a slightly increased affinity for methylene-blue, and responded to the metal affinity test; a slightly deeper Turnbull's blue was obtained on the carboxylic cotton-dextrin prepared from the aldehydic cotton-dextrin than on that prepared from the cotton piece. A solution of half the above concentrations of permanganate and acid did not convert the aldehydic cotton-dextrin into a detectable amount of carboxylic cotton-dextrin.

Dyeing properties of carboxylic and aldehydic cotton-dextrin material

Equal weights of carboxylic cotton-dextrin material, aldehydic cotton-dextrin material, and ordinary cotton piece were dyed in the same bath, with representative dyestuffs of the direct cotton, basic, sulfur, sulfur-vat, indigoid-vat, and anthraquinone-vat classes.

Direct cotton dyestuffs.—The dyestuffs employed were Chlorazol Fast Orange DS (stilbene compound), Chlorazol Pink YS (monoazo compound), Chlorazol Fast Helio BKS and Chlorazol Sky Blue FFS (disazo compounds), and Chlorazol Green BNS (trisazo compound); these were dyed as 1% shades (calculated on weight of material). In every instance the aldehydic cotton-dextrin material had a slightly less affinity, and the carboxylic cotton-dextrin material considerably less affinity, than cotton for the dyestuffs. This was particularly marked with the mono- and dis-azo compounds.

Basic dyestuffs.—Two sets of comparative dyeings were performed: (*a*) previously mordanting the materials with 5% of tannic acid and 2½% of tartar emetic: (*b*) dyeing directly without previous mordanting. The representative dyestuffs employed were Acridine Orange RS, Rhodamine BS, Safranine TS, Magenta PS, Methylene Blue 2BS, and Malachite Green AS crystals in amounts representing ½% on the weight of material. In the dyeings under conditions (*a*), there was no difference between the strengths or tones of shade obtained on the three different materials, showing that cotton fabrics containing some aldehydic and carboxylic cotton-dextrin can be dyed evenly with basic colors on a tannin mordant. Under conditions (*b*), however, the carboxylic cotton-dextrin material had much greater affinity for all of the basic colors employed. This was particularly marked with Acridine Orange RS, Malachite Green AS crystals, and Methylene Blue 2BS. With all the above basic colors with the exception of Methylene Blue 2BS, the aldehydic cotton-dextrin material had slightly less affinity than cotton; it was dyed to the same strength of shade as the cotton with Methylene Blue 2BS. The dyeings were commenced cold and gradually warmed up to 60° during 20 minutes.

Sulfur dyestuffs.—Dyeings were performed by the usual procedure with sodium sulfide and soda ash present, with Thionol Brilliant Green GS, Thionol Sky Blue 6BS, Thionol Brown GS, and Thionol Direct Blue RLS. The depth of shade on the carboxylic cotton-dextrin material was less than that on the cotton and aldehydic cotton-dextrin material—this was particularly noticeable with the more easily reducible dyestuffs, Thionol Brilliant Green GS and Thionol Sky Blue 6BS. The depth of shade on the aldehydic cotton-dextrin material was slightly less than that on the cotton. The amounts of dyestuffs employed represented 3% of the weight of material present. This effect was slightly less marked when the materials were dyed with Hydron Blue R but was noticeable.

Indigoid and anthraquinone vat colors. — The three materials were dyed by the appropriate methods with Durindone Blue 4BCS, Durindone Red 3BS, Caledon Orange 2RTS, Caledon Blue RCS, and Caledon Dark Blue BMS, and the same effect occurring with sulfur colors was again noticeable, *i.e.*, the depth of shade on the carboxylic cotton-dextrin material was less, and that on the aldehydic cotton-dextrin material slightly less, than that on the normal cotton piece. This effect was most pronounced with Caledon Orange 2RTS and Caledon Blue RCS. The amounts of dyestuff employed represented 10% of the weight of material.

Best conditions for selective tests for carboxylic cotton-dextrin in the presence of aldehydic cotton-dextrin and non-degraded cotton

General method.—The carboxylic cotton-dextrin is detected by reason of its affinity for metals from solutions of their salts. The presence of the metal on the material is then manifested by characteristic color reactions. It is also possible that this method could be employed for the determination of carboxylic cotton-dextrin by means of the determination of combined metal.

(A) The following tests are satisfactory when it is known that no raw or grey cotton is present, and are based on the above general method. In each test, separate pieces of normal bleached cotton piece, carboxylic cotton-dextrin material, and aldehydic cotton-dextrin material were immersed in the same bath.

(1) *Lead chromate test.*—The three pieces of material were immersed in a 1% lead acetate aqueous solution for 5 minutes at room temperature and then thoroughly washed in several changes of warm water, and subsequently immersed in a 1% solution of sodium chromate for 5 minutes at room temperature, when the material was finally washed in cold water. The cotton piece was tinted faintly yellow, and the aldehydic cotton-dextrin material was a cream color, while the carboxylic cotton-dextrin material was colored a deep yellow.

(2) *"Turnbull's blue" test.*—This was found to be the most satisfactory and sensitive method for detecting carboxylic cotton-dextrins in various stages of degradation and in small amounts. The materials were immersed in a 1% aqueous solution of ferrous sulfate at room temperature for 10 minutes, then thoroughly washed in several changes of warm water, and subsequently immersed in a 1% solution of potassium ferricyanide for 5 minutes and finally washed. The cotton was then tinted faintly blue and the aldehydic cotton-dextrin still more faintly blue, while the carboxylic cotton-dextrin material was colored a very deep blue.

(3) *"Prussian blue" test.* — The materials were immersed in a 2% aqueous solution of ferric chloride for 10 minutes at room temperature, thoroughly washed in cold water, and then immersed in a 2% aqueous solution of potassium ferrocyanide at room temperature for 5 minutes and finally washed. The cotton piece was then tinted pale blue, the aldehydic cotton-dextrin material faintly blue, whereas the carboxylic cotton-dextrin material was colored a deep blue.

(4) *Production of "Turnbull's blue" by reduction of some ferric chloride and subsequent development with potassium ferricyanide.*—(*a*) The three pieces of material were immersed at room temperature in a 2% aqueous solution of ferric chloride for 1 hour, then washed thoroughly in cold water and subsequently immersed in a 2% aqueous solution of potassium ferricyanide for 10 minutes. The cotton piece was tinted faintly blue, the aldehydic cotton-dextrin material was almost imperceptibly blue, whereas the carboxylic cotton-dextrin material was a definite blue shade of medium depth.

(*b*) After immersion in a 2% aqueous solution of ferric chloride for 1 hour at room temperature, the three pieces of material were thoroughly washed in hot water (60°) and entered into a 2% aqueous solution of potassium ferricyanide and eventually washed in cold water. The cotton piece assumed a pale greenish tint, the aldehydic cotton-dextrin material an almost imperceptible blue tint, and the carboxylic cotton-dextrin a fairly deep blue coloration.

These two procedures (*a*) and (*b*) are tedious but interesting, since they are based on both the reducing and metal affinity properties of carboxylic cotton-dextrin.

(5) *Ferric thiocyanate test.*—The materials were immersed in a 2% aqueous solution of ferric chloride at room temperature for 10 minutes, then thoroughly washed in cold water and immersed in a cold 2% solution of potassium thiocyanate. The carboxylic cotton-dextrin material immediately became colored a deep reddish-brown, while the cotton piece and aldehydic cotton-dextrin material were only slightly stained. The color on the carboxylic cotton-dextrin material washed off in water, however, so that no permanent records could be kept from this test.

In order that the above tests should be selective, it was necessary to wash the material very thoroughly in several changes of water after treatment in the first solution.

Test for detecting carboxylic cotton-dextrin or aldehydic cotton-dextrin

The three pieces of material were boiled for 5 minutes in Fehling's solution, containing about 17 g. of copper sulfate, 30 g. of sodium hydroxide, and 85 g. of Rochelle salt (sodium potassium tartrate) per liter, and then washed off in water. The carboxylic cotton-dextrin and aldehydic cotton-dextrin material were both stained a reddish-brown color, while the cotton piece was tinted faintly blue. If such a reddish stain is obtained and the positive tests for carboxylic cotton-dextrin are not fulfilled, then the presence of aldehydic cotton-dextrin is inferred. It does not appear possible to determine qualitatively whether both carboxylic and aldehydic cotton-dextrin are present.

(B) Detection of carboxylic cotton-dextrin in the presence of grey or raw cotton

The normal grey cotton encountered has a slight reducing action on Fehling's solution, and an affinity for basic

dyestuffs and also for metals from solutions of their salts. It was found that by boiling for about 10 minutes in an aqueous solution containing 3 g. of Perminal KB and 5 g. of sodium carbonate per liter, and finally washing in hot water, the grey cotton did not reduce Fehling's solution and had only a slight affinity for metals from their salts.

When grey cotton piece containing carboxylic or aldehydic cotton-dextrins (prepared as described previously) was subjected to this light scouring treatment, these dextrin substances were not removed to any detectable extent as shown by the Fehling's solution and metal affinity tests. Of these latter series of tests it was found that the one depending on the development of "Turnbull's blue" was the most suitable. A practical procedure for the detection of carboxylic cotton-dextrin or aldehydic cotton-dextrin in fabrics or mixed yarns which may consist of grey as well as of bleached cotton is therefore as follows:

The fabric or yarn is boiled for about 10 minutes in an aqueous solution containing 3 g. of Perminal KB and 5 g. of soda per liter, and finally washed in hot water. This treatment should remove any filling which would interfere with the selectivity of the tests. A portion of the material is then boiled for 5 minutes in Fehling's solution. If reduction occurs, to give a reddish deposit of cuprous oxide on the material, either carboxylic or aldehydic cotton-dextrin or both are present; they may be present on bleached or grey cotton. Non-degraded bleached or grey cotton, however, does not give this test after the light scour. If reduction of Fehling's solution occurs, then the following test is performed.

A further portion of the scoured material, together with normal cotton as a blank, is immersed in a 1% aqueous solution of ferrous sulfate at room temperature for 5 minutes, washed in hot water (about 70°) and then in several changes of warm water, when it is immersed in a 1% solution of potassium ferricyanide for 5 minutes at room temperature and finally washed in hot water. If the material is colored a deep blue, then carboxylic cotton-dextrin is present either on grey or bleached cotton; grey cotton containing aldehydic cotton-dextrin or in a non-degraded condition is much less deeply colored, and bleached cotton containing aldehydic cotton-dextrin, or in a non-degraded condition, is only faintly colored. (If grey cotton has not been previously boiled out with the dilute soda ash and Perminal, it acquires a blue shade.) The above procedure is discriminatory, and clearly showed the presence of carboxylic cotton-dextrin in cotton tendered by exposure to sunlight.

The lead chromate test (1) was fairly selective, but the grey cotton was tinted more than the bleached; the "Prussian blue" test (3) was somewhat less selective owing to the same cause. The presence of grey cotton vitiated test (4) since there was not a wide enough difference in depth of color between grey cotton or aldehydic cotton-dextrin on grey cotton, and carboxylic cotton-dextrin on grey cotton. It was confirmed that this test was of very good selectivity where only bleached cotton was concerned.

Tetrazotized benzidine has somewhat more affinity for carboxylic cotton-dextrin than for aldehydic cotton-dextrin or non-degraded cotton, but on coupling with β-naphthol the differences in the depth of shade are not sufficiently marked to enable a selective test to be devised on these lines. The methylene-blue test was found to be equally lacking in selectivity, since the grey cotton after the light scouring acquires a medium depth of color.

Effect of the twist of cotton yarns on the metal affinity test

The five selective tests based on the affinity of carboxylic cotton-dextrin for metals from solutions of their salts were applied to both single and twofold bleached cotton and grey cotton yarn, and also these yarns containing carboxylic and aldehydic cotton-dextrins. It was found that there was little or no difference between the depths of shade developed on the single and twofold yarns. The twist of the yarn does not therefore influence the efficacy of the tests. This conclusion was also arrived at from the Fehling's solution test.

Testing of dyed material

It was found that when aldehydic and carboxylic cotton-dextrin materials were subjected to the following three stripping processes, the tests set out above showed that these dextrins were still present in the material in an apparently unchanged condition and amount. If dyed material can therefore be reasonably well stripped by any of these three procedures, the tests of aldehydic and carboxylic cotton-dextrins can then be applied, and if they do not indicate the presence of either dextrin, it can be considered that neither was present in the dyed material.

Stripping methods: (*a*) 0.5% solution of sodium hydrosulfite and a little ammonia at 40° for ½ hour. (*b*) 0.1% solution of titanous sulfate or chloride at 40° for ½ hour. (*c*) 1% solution of soap and 0.5% of soda ash, together with decolorizing charcoal (Carboraffin at the boil for ¼ hour.

Reactivity of carboxylic cotton-dextrin with salts of metals

Cotton piece, aldehydic cotton-dextrin material, and carboxylic cotton-dextrin material were immersed separately in a neutral 2% aqueous solution of ferrous sulfate and warmed to 30°. Tests with B.D.H. Universal Indicator showed that the solution in which the carboxylic cotton-dextrin was immersed became definitely acid ($p_H > 3.0$), while the solutions in which the other two materials were immersed became only slightly acid (p_H about 6.0).

Summary

Typical "oxycelluloses" and "hydrocelluloses" have been prepared by different methods.

Their dyeing and chemical properties have been examined, and interpreted by conceptions of their molecular structures which have been tentatively advanced. A new and more precise terminology based on these representations is suggested, and if adopted should obviate a great

deal of confusion which is so liable to occur in this subject. The term "aldehydic cotton-dextrin" is suggested for "hydrocelluloses" which exhibit reducing properties, but no affinity for metals from solutions of their salts, or for basic dyestuffs. The term "carboxylic cotton-dextrin" is suggested for "oxycelluloses" which exhibit reducing properties, a marked affinity for metals from solutions of their salts and for basic dyestuffs, and a poor affinity for direct cotton dyestuffs.

New discriminatory tests based on a general "metal affinity method" have been devised for the detection of carboxylic cotton-dextrin in the presence of cotton and aldehydic cotton-dextrin. General procedures for the detection of the presence of either carboxylic cotton- dextrin or aldehydic cotton-dextrin in mixed cotton fabrics containing grey cotton, or in dyed fabrics which can be stripped fairly readily, have been evolved.

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Dyehouse Laboratories,
Imperial Chemical Industries (Dyestuffs),
Blackley, Manchester

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THE ECONOMIC PRODUCTION OF TRUE SHADES

(Continued from page 352)

Of the non-ferrous alloys those with nickel, copper, or aluminum bases find the most important uses in the textile industry. In addition pure nickel, pure lead, and pure tin have their special uses. (By pure is meant unalloyed. analysis would disclose traces of impurities).

Yellow Brass

Copper	58.5% to 61.5%
Lead	1.5 to 2.50
Iron, Max.	.15
Impurities	.35
Remainder	Zinc
Tensile strength	40,000 lbs.

Monel

Nickel	67%
Copper	28%
Other metals, chiefly lead, etc.	5%
Tensile strength	100,000 lbs.

Phosphor Bronze

Copper	88.0% to 90.0%
Tin	10.0 to 12.0
Phosphorus	.10 to .30
Lead, Zinc, and Impurities	.50
Tensile strength	35,000 lbs.

Manganese Bronze

Copper	53.0% to 62.0%
Zinc	38.0 to 47.0
Manganese	3.0
Lead, Max.	.15
Tensile strength	70,000 lbs.

Aluminum Bronze

Copper	85.0% to 87%
Tin, Max.	.50
Aluminum	7.0 to 9.0
Iron.	.50
Impurities	.25
Tensile strength	65,000 lbs.

It will be noted in studying these formulae that no index is shown that will guide either the chemist or the dyer in the proper choice of a metal and laboratory tests prove very little, as the element of time is a very important factor, as is the mass of the metal. Then, too, there are many unsatisfactory conditions aside from metal influence on a particular dyestuff (which may be disclosed through laboratory experimentation). Smuttiness, the difficulty of washing down the kettle, discharge stains, streakiness readjustment or change in the alloy through strain, heat, and acid or alkaline concentrations, or combinations of all three to produce structural weakness with resultant high repair costs, electrolysis through improper metal combinations or through faulty workmanship of the alloy (especially true of the stainless steels), and other conditions unfavorable to satisfactory results. So it can be seen that a metal of high acid or alkalae resistance or lack of color influence to a particular dyestuff classification may prove anything but satisfactory in actual practice.

Therefore, it should be cautioned (but we do not discourage experimentation, except that we do wish to point out that it often proves discouraging to management when present with the actual costs) that those looking forward to the advantages accruing from the use of the newer alloys should proceed slowly in their own efforts at construction and rely upon the accumulated knowledge and experience of the manufacturers of equipment, at least for such time as the definite knowledge as to constructional difficulties and deleterious process reactions are so little a part of common knowledge.

Georgia Tech Notes

Messrs. Williams and Schroder, of the General Dyestuff Corporation, recently met with the members of the senior textile class at which time Mr. Williams made a very interesting talk covering the application of naphthol colors and followed this with a practical machine demonstration.

Mr. John C. Robertson, of the Peroxide Bleaching Division, du Pont Company, gave a talk to the students discussing the use and application of peroxides in bleaching.

Messrs. Taylor and Viera of the Dyestuffs Division, du Pont company were also recent visitors to the institution. Mr. Viera spoke on the use of vat colors in dyeing and printing.

At the annual Honor Day exercises, April 28th, senior textile students receiving awards were as follows: Alva Dean Zellner—the National Association of Cotton Manufacturers medal for excellence in scholarship; J. Alex Fife—the Cotton Manufacturers medal for general scholarship and particular application in the textile department.

Tomalino Silk Dye Works

F. A. Tomalino has purchased the assets of the Northern Silk Dye Works and in the operation of the plant will be associated with him Mr. Reed, formerly a hosiery manufacturer. After the plant has been renovated and modern dyehouse machinery installed the new firm will specialize on skein, piece and hosiery in silk, rayon and mixed fabrics, converting and finishing.

Sartorius Analytical Balances

Pfaltz and Bauer, Inc., 300 Pearl St., New York City, have announced the publication of a new catalog on "Sartorius Analytical Balances." They call attention to several innovations and interested persons who use balances in textile laboratory work may obtain copies of the catalog.

Cibanone Pastes

Cibanone Green 4G (P) double paste and Cibanone Green 5G paste are two new vat dyes of the Society of Chemical Industry in Basle, of which the type 4G double paste is said to be distinguished by very good fastness to light, washing and chlorine.

According to the distributors both the new dyestuffs are suited for printing cotton, rayon and pure-dye silk.

It is said that Cibanone Green 4G (P) double paste finds most appropriate use where the greatest fastness requirements are necessary, such as upholstery, draperies and shirtings.

CLASSIFIED

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

Turn those odd lots of dyestuff into cash. Opportunity to liquidate your surplus stock of dyes. Let me know what you have on hand and I will put you in contact with a buyer on a 10% commission basis. Inquiries for job lots also solicited—Charles J. Rupp, (formerly of Kalle-Newport-DuPont), 420 State St., Brooklyn, N. Y.

POSITION WANTED—Cotton and Rayon Piece Dyer. Twenty-five years' practical experience in processing and dyeing. Capable of taking charge of any dye-house and producing results. Had charge of two large dye-houses. References first class. Will go anywhere. Address Box No. 776, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

TEXTILE SCHOOL GRADUATE—Eleven years' experience in both practical and laboratory printing and dyeing of cotton, rayon, wool and acetate silk; also dyestuff experience both laboratory and sales. Executive ability. Desires new connection. Address Box No. 777, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

CELANESE AND RAYON DYER desires position. Is thoroughly experienced in every phase of the work on piece goods. Can handle boil-off. Address Box No. 778, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

TEXTILE CHEMIST AND ANALYST—Graduate of Lowell Textile Institute, desires position in mill laboratory or with chemical concern catering to the textile trade. Two years' experience in the laboratory of one of the leading textile manufacturers. Can supply best of references. Address Box No. 779, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

WANTED—Expert hosiery dyer on both paddle and rotary type machines. Box No. 780, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.